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ISOTOPE WORKSHOP III

24–28 June, 1996, Budapest, Hungary

Short papers and abstracts

Edited by: **ATTILA DEMÉNY** and **ISTVÁN FÓRIZS**

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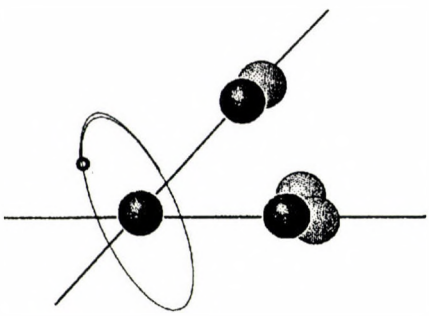

Organizers:
Laboratory for Geochemical Research, Hungarian Academy of Sciences
International Isotope Society (established in 1992, Poland)

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FOREWORD

The history of Isotope Workshops began in 1992 when the first one was held in Lublin, Poland. Thanks to the international attention, a new society named International Isotope Society was established afterwards whose members were workshop participants. The 2nd Isotope Workshop was already organized under the umbrella of IIS in Książ (near Wrocław), Poland, and consequently attracted researchers from more countries. The present meeting, Isotope Workshop III - whose abstracts comprise this volume -, takes place in Budapest. As the fame of the Workshop spread with time, researchers from more and more countries showed interest in the meeting. The organizers intended to enhance the international character of the meeting and invited well known scientists to chair some of the most important sessions. Their intention was further supported by the Hungarian Academy of Sciences that provided financial as well as organization help.

The Workshop is divided to 6 sessions: Paleoenvironmental indicators, Paleoclimatology and isotope hydrology, Isotopes and the human environment, Isotope geochemistry of sediments, High temperature geological processes, and Recent technical developments. Accordingly to the present-day need of isotope research, most of the presentations deals with environmental problems like air pollution sources, and groundwater flows. Beside presentations of isotope geochemical studies of academic interest - that, however, delight many of us engaged in the world of pure science -, the participants gain insight into the recent technical developments of isotope measurements as well as production of isotopically labelled compounds.

The abstracts of oral and poster presentations are compiled in this volume in the order of the first authors' names. The abstracts were inserted in "camera-ready form", thus the authors hold full responsibility for their contents. An author index list and a keyword index list are given at the end in order to help the reader to find the papers of her/his interest.

Finally, the editors wish the reader a joyful time while browsing through the newest results of the Isotope Workshop III participants.

Attila Demény and István Fórizs
editors

CONTENTS

NITROGEN ISOTOPE EXCHANGE BETWEEN NITRIC OXIDE AND NITRIC ACID

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KEYWORDS: $^{15}N/^{14}N$ isotopic exchange; NO - HNO_3 system; kinetic equation, N_2O_3 , ^{15}N separation.

Chemical exchange of nitrogen between nitric oxide and concentrated nitric acid provides the bases for the nitrogen isotope separation process that is most widely used at the present time, i.e., the method of Spindel and Taylor (1955).

The exchange rate law experimentally observed for $^{15}N/^{14}N$ exchange in NO - HNO_3, at low nitric acid concentration, both at atmospheric pressure (Axente and Piringer, 1971) and at low pressure of NO (Jordan and Bonner, 1973):

$$R = k\ [H^+]\ [NO_3^-]\ [HNO_2]$$

is identical to the rate law for reaction between NO and HNO_3, when HNO_2 is formed.

It is important to know what happens in the nitrogen exchange between NO and HNO_3 at acid concentrations higher than 1-2 $M.l^{-1}$, when in the liquid N_2O_3 appears instead of HNO_2. We report here the results of experiments designed to answer this question.

In the kinetic measurements presented in this paper the HNO_3 solution was preequilibrated chemically with NO gas, and the system was then desequilibrated by addition af a small quantity of $H^{15}NO_3$ solution 18.55 at.% ^{15}N. In order to eliminate the possibility that phase mixing imposes a rate limitation aqueous solutions of nitric acid were brought into contact with NO gas by vibration of a reaction cell, similar with that described by (Jordan and Bonner, 1973) and exchange of nitrogen was followed by

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sampling the gas phase for mass spectrometric analysis.

The rate of NO absorption in nitric acid solution, using the same reaction cell as for isotopic exchange reaction, was also measured.

The exchange data were treated by use of the McKay law in the form:

$$-\frac{d \ln (1 - F)}{dt} = \frac{A + B}{A \cdot B} \qquad (1)$$

where: - R is the nitrogen isotope exchange rate ($M.l^{-1}.s^{-1}$)

- F is the exchange fraction at time t:

$$F = \frac{X_t - X_0}{X_\infty - X_0}$$

(The values of X represent the ^{15}N content of NO at time 0, t and ∞, isotopic equilibrium).

$$-A = [HNO_3]_i - 2/3\,[N_2O_3]\ ;\ (M.l^{-1}) \qquad (2)$$

$[HNO_3]_i$ is the initial concentration of nitric acid, ($M.l^{-1}$).

$[N_2O_3]$ is the equilibrium dinitrogen trioxide concentration in the liquid, ($M.l^{-1}$).

$$-B = \frac{NO_G + 1/4\ NO_L}{V} + 2\,[N_2O_3]\ ;\ (M.l^{-1}) \qquad (3)$$

NO_G and NO_L represents nitric oxide quantity (M) in gas, respectively in liquid phase, and V is the liquid volume (l) in reaction cell.

The results of nitrogen exchange kinetic measurements are summarized in Table I; for $[HNO_3]_i$: 1.5 ÷ 2.5 $M.l^{-1}$ R was determined at 730 torr NO and for $[HNO_3]_i$: 3 ÷ 4 $M.l^{-1}$ at 91.25 torr NO pressure.

We note the approximate constancy of the $\frac{R}{[HNO_3]_e^2 \cdot [N_2O_3]}$ as shown in column 5, Table I, which would imply a rate law:

$$R = k\,[HNO_3]^2\,[N_2O_3] \qquad (4)$$

for $^{15}N/^{14}N$ isotopic exchange in NO - HNO_3 system, in the concentration range 1.5 ÷ 4 $M.l^{-1}$ nitric acid.

From eq. (4) it is obvious the role of N_2O_3 in nitrogen isotopic exchange at nitric acid concentration higher than 1.5 $M.l^{-1}$.

TABLE I

Results of $^{15}N/^{14}N$ exchange kinetic measurements

T = 25°C

$[HNO_3]_i$	R	$[HNO_3]_e$	$[N_2O_3]$	$\frac{R}{[HNO_3]^2_e \cdot [N_2O_3]}$	p_{NO}
$(M.l^{-1})$	$(M.l^{-1}.s^{-1})$	$(M.l^{-1})$	$(M.l^{-1})$		(torr)
1.5	$6.21 \cdot 10^{-3}$	1.400	0.1500	0.021	730
2.0	$1.49 \cdot 10^{-2}$	1.885	0.1725	0.024	730
2.5	$2.31 \cdot 10^{-2}$	2.370	0.1850	0.022	730
3.0	$8.83 \cdot 10^{-3}$	2.968	0.0485	0.021	91.25
4.0	$2.03 \cdot 10^{-2}$	3.961	0.0578	0.023	91.25

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SYNTHESIS OF ^{15}N LABELLED COMPOUNDS

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KEYWORDS: ^{15}N labelled compounds, ^{15}N nitrites, ^{15}N nitrates, ^{15}N ammonium salts, ^{15}N urea.

A plant consisting of two columns for ^{15}N separation by isotopic exchange between nitric oxides and nitric acid solution, so called Spindel-Taylor (1955) process, is operating at Cluj. The product, up to 99,9% ^{15}N atom, can be extracted both as nitric oxides (NO_x) or approximately 10 M nitric acid solution, have to be converted in the desired labelled compounds. Large quantities of ^{15}N are required mainly for labelled fertilizer (3 - 10% ^{15}N) for agricultural research with. For biological or structural studies where NMR technics are involved a higher ^{15}N content (95 - 99%) must be used.

Nitric oxides can be separated by distillation to produce NO or converted into simple molecules by chemical reactions:

$$
{}^*NO_x \begin{cases} \xrightarrow[750\,^\circ C]{Cu} {}^*N_2 \\ \xrightarrow[Mn,\ 500\,^\circ C]{H_2} {}^*NH_3 + H_2O \\ \xrightarrow{\text{excess } O_2} {}^*NO_2 \\ \xrightarrow{O_2} {}^*N_2O_3 \xrightarrow{NaOH\ (KOH)} Na{}^*NO_2\ (K{}^*NO_2) \end{cases}
$$

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Nitrogen is obtained by copper powder reduction is a silica combustion tupe at a flowrate of 1 - 3 l/hr· cm^2 cross section the nitrogen being storred in glass ampoules or stainless steel cylinder cooled with liquid nitrogen. By reduction of NO_x with excess hydrogen (NO : H_2 = 1 : 50) on metalic manganese granules (0.2 - 1.25 mm) in a silica tube ammonia is obtained (Axente and co., 1972). The nitrites were obtained by absorption of N_2O_3 in sodium or patassium hydroxides. In the reaction NO is always in great excess to avoid nitrate formation. The water is vacuum evaporated and the unreacted hydroxide is removed by ethanol washing. The product contains some nitrate.

The nitrates are obtained by neutralization of H^*NO_3 with hydroxides or by carbonates. Thus labelled compounds like $NH_4{}^*NO_3$, K^*NO_3, $Ca(^*NO_3)_2$, etc. are obtained. Ammonia produced by Dewarda alloy can be absorbed in acid solutions to produce ammonium salts, such as $^*NH_4Cl$, $^*NH_4{}^*NO_3$, $(^*NH_4)_2SO_4$, etc.

The labelled ammonia was converted in urea by reaction (Frantz and Applegath, 1961):

$$CO + S + 2{}^*NH_3 \text{ --------> } H_2{}^*N\text{-}CO\text{-}{}^*NH_2 + H_2S$$

There used two stainless steel reactors of 275 and 1200 cm^3 to produce approximately 10 and 45 g respectively per run. The autoclave was charged in the ratio S : $^*NH_3$: CO of 1 : 1.40 : 1.35, the required elemental sulfur and methanol (37 and 160 cm^3 respectively) were introduced, the reactor was frozen with liquid nitrogen and evacuated. Labelled ammonia was measured by a know volume cylinder, the temperature was brought to room temperature and carbon monoxide was added to 35 atm. The autoclave was heated to 110 - 120°C (Iovi and co., 1964, 1965) for two hours. The unreacted and product gases (CO, COS, H_2S, NH_3) were evacuated with care to recover ammonia. The reactor was opened and methanol was evaporated. The urea was dissolved in water and filtered to remove sulfur and finally recristalized from ethanol. The yield of 90 - 95% based on labelled ammonia were obtained.

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Application of Chlorine-36 in Studies of Deep Groundwaters in Geothermal Areas in Western Turkey and the Great Hungarian Plain

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Keywords: Chlorine-36 dating, geothermal water, Anatolia, Great Hungarian Plain

For groundwaters of tectonic active regions and of great basins the problem of the determination of the residence time occurs, as the usually applied isotope techniques are often not appropriate because of

I) the long residence time,
II) the high amount of water-rock interaction,
III) the underground production of nuclides in crystalline fissured rocks in geothermal conditions,
IV) the occurrence of highly saline and hot waters affected by water-rock interaction processes.

In tectonic active areas also the high fluxes of CO_2 influence the groundwater chemistry. The application of the chlorine-36 method in such areas looks very promising.

Within this presentation the interpretation of selected results of chlorine-36 determinations of several study areas along the North Anatolian Fault zone and of the Great Hungarian Plain (GHP) are discussed. Main effects of underground processes which affect the ^{36}Cl in deep groundwaters are:

(1) underground production,
(2) leaching of rock salt (including fluid inclusions) due to water rock interaction processes,
(3) dissolution of limestones especially in areas of high CO_2 activity related to thermometa-morphic process
(4) processes of mixing of fluids with different origin/evolution with different chloride concentrations and ^{36}Cl ratios which are moved by the active tectonic processes.

By considering for each area the sources of chlorine-36 and the water-rock interaction processes with respect to the chloride cycle additional information on the ongoing evolution of the groundwaters and the circulation as also of the ranges of residence times were gained. Dating with ^{36}Cl is only possible if the local input ratio and exact evolution (and the rock environment along flow path and including the geological evolution of the area) is known.

Additional information, independent hydrodynamic and coupled geothermal modelling as also the results of environmental isotopes give additional support to the achieved interpretation.

Method, experiences and results of K-Ar dating of alkali basalt volcanism in central and southern Slovakia (West Carpathians)

Balogh, Kad[1] *., Konečný, V.*[2]*, Orlický, O.*[3]*, Lexa, J.*[2]*, Vass, D.*[2]

Key words: K-Ar dating, excess Ar, isochron ages, reliability, alkali basalt, central and southern Slovakia

Alkali basalt volcanism in central and southern Slovakia was active since the upper Miocene to Quaternary time They are situated mostly on stable blocks bordering young extension basins during the thermal stage of their subsidence. A local updoming contemporaneous with alkali basalts in the Cerová vrchovina area may indicate the presence of a spatially limited mantle plume responsible for generation of alkali basalt magmas. The basaltic areas are shown in Fig. 1, their geological setting and palomagnetic polarity is summarized by Konečný et al. (1995) and Orlický et al. (1995).

The first K-Ar ages on alkali basalts from central Slovakia were published first by Kantor and Wiegerová (1981), Balogh et al. (1981) and Kantor at al. (1984). The data presented by the two groups were concordant, but due to the presence of excess Ar they were frequently older than the geological age. The isochron method has been applied first for a set of unquestionably coeval whole rock samples. However, it was usually difficult to collect rock samples with sufficiently different K concentrations from the same lava flow, dike or neck. If the K and excess Ar concentrations were similar in the rock samples selected for the isochron method, but the atmospheric Ar concentrations showed a significant variation, then a good linear arrangement (mixing line) could be obtained in the isochron diagram, but the defined "age" was erroneously old.

In order to overcome this trouble, according to Fitch et al. (1976), the isochron method was applied for different fractions of a single piece of rock. By crushing the basalt to below 0.16 mm or 0.1 mm and using magnetic and heavy liquid separation, usually a 2-fold difference in the K concentrations could be achieved. It has been noted, that in the Cerová vrchovina area excess Ar is either distributed more or less uniformly in the rock, or it is concentrated in the less magnetic part of the fraction of highest density. Sometimes better fit was obtained in the $^{40}Ar(rad)$ - ^{40}K diagram. This can happen, if the introduction of additional atmospheric Ar in the rock modifies the Ar isotopic composition, but does not change the uniform distribution of excess Ar.

In few cases the points representing the fractions of the rock did not fit well a straight line in the isochron diagrams (Fig. 2), indicating, that concentration and/or isotopic composition of the initial Ar was not uniform, or additional atmospheric Ar was introduced in the rock at a later time of its history. The randomly scattered points show, that K-Ar ages are unreliable (i. e.

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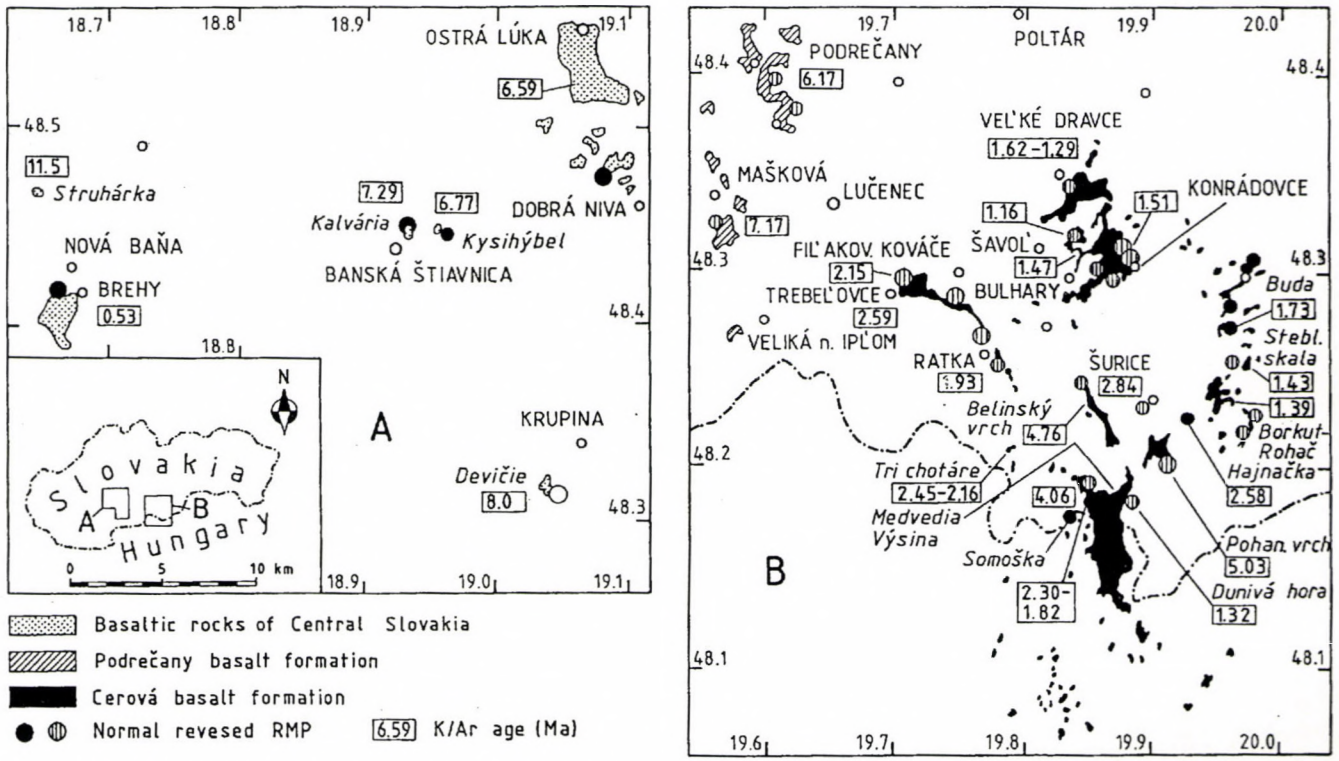

Fig. 1. Sketch map of the alkali basaltic areas in central (A) and southern (B) Slovakia

this rock is unsuitable for dating). This is disappointing, but it is more serious mistake, if an erroneous isochron age is accepted as real geological age.

A systematic study has been started in order to obtain the real geological age for basalts with inhomogeneous initial Ar isotopic composition and to recognize the unreliability of apparently good isochron ages. The alkali basalt of Šomoška has been selected for this purpose (Balogh et al., 1994). It has been shown, that isochron ages obtained by the $^{40}Ar/^{36}Ar$ - $^{40}K/^{36}Ar$ and $^{40}Ar(rad)$ - ^{40}K diagrams can be equal, but erroneous, if there is a linear relation between the excess Ar and K concentrations and it fulfils one of the following conditions:

1. At zero K concentration the excess Ar concentration is also zero.
2. The atmospheric Ar concentration is constant.

In these cases the bias between the apparent isochron age and the real age will be proportional with the Ar(ex)/K ratio. Considering, that in case of uniform initial Ar isotopic ratio the excess Ar and atmospheric Ar concentrations are proportional, i. e. the atmospheric Ar content may inform us on the possible excess Ar concentration, the following method has been adopted for the evaluation of isochron diagrams:

1. If the points fit well a straight line and the K concentrations are sufficiently different, the correlation of atmospheric Ar and K concentrations is examined. In lack of correlation (at least for a part of the points defining the isochron), the isochron age can be accepted as real geological age.

Fractions	Age	Interception
o 0.1 - 0.15 mm	4.40 ± 0.89 Ma	302 ± 11
■ 0.043-0.1 mm	5.00 ± 1.54 Ma	303 ± 18
All	4.64 ± 1.36 Ma	304 ± 16
Selected	4.06 ± 0.06 Ma	310.8 ± 2.2

Fractions	Age	Interception
o 0.1 - 0.15 mm	4.31 ± 0.85 Ma	0.49 ± 0.55
■ 0.043-0.1 mm	6.02 ± 0.90 Ma	-0.25 ± 0.49
All	5.23 ± 0.84 Ma	0.057 ± 0.49
Selected	4.08 ± 0.03 Ma	0.54 ± 0.015

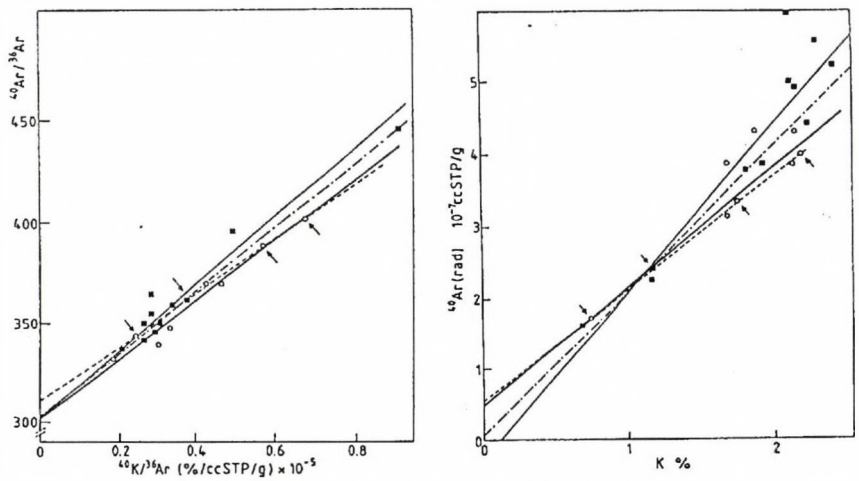

Fig. 2. Fractions of the Šomoška basalt in the isochron diagrams

2. If the points are randomly distributed in the diagrams, fractions with similar and low atmospheric Ar concentrations are selected. There is a chance, that these points will define a reliable isochron. E. g. 4 fractions of the Šomoška basalt with Ar(atm) concentrations in the $1.06\text{-}1.11 \times 10^{-6}$ cc STP/g range (marked with arrows in Fig. 2) defined excellent isochron ages.

K-Ar ages characterizing the alkali basalt volcanism in central and southern Slovakia and evaluated with the method described above are shown in Fig. 1. The oldest basalt/basanite volcanic products are in central Slovakia, but members of the Podrečany basalt formation are only little younger. The genetic type of the oldest basalt (Struhárka, 11.5 Ma) is under study. Alkali basalts and basanites of the Cerová formation are younger (Fig. 1). Cinder cone Pútikov vrš ok and related lava flow in the western part of the Central Slovakia Neogene Volcanic Field is the youngest alkali basalt in Slovakia. As the lava flow lays over the Riss terrace of river Hron, its age is probably younger than the conventional K-Ar age of 0.53 Ma, the bias is likely caused by undetected excess Ar.

Acknowledgement: K-Ar dating was supported partly by the Hungarian National Science Foundation (OTKA) projects No. 1180 and T 014961.

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Isotope geochemical and pollution study of groundwaters in the area between the Rivers Danube and Tisza

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Keywords: isotope hydrogeology, stable oxygen isotope, radiocarbon, nitrate pollution

INTRODUCTION

For drinking water purposes in the area of the Great Hungarian Plain mostly groundwater resources are used. The central part of the area between the Rivers Danube and Tisza (part of the Great Hungarian Plain) is a regional recharge area. The infiltrating water flows towards the rivers depending on the topography and geology of the area. The rivers discharge this groundwater flow system. These groundwaters under the regional recharge area are very vulnerable for the potential surface pollutions, e.g. nitrate, heavy metals, etc. Stable and radioactive isotope data of oxygen, hydrogen and carbon have been applied for investigating the detailed circulation system, and the mixing process of surface and subsurface waters. For studying the infiltration and migration of the pollutants nitrate, nitrite and ammonium data have been evaluated and compared with the isotope data.

METHODS and RESULTS

Stable oxygen and hydrogen isotopic, radiocarbon, tritium and water chemical data have been used from the hydrological data base of VITUKI (Research Center for Water Resources), and samples have been taken from 20 wells and analyzed for stable oxygen and hydrogen isotope composition, chemical contents.
The δD values have been plotted vs. $\delta^{18}O$ values and compared with global meteoric water line (MWL, $\delta D = 8 * \delta^{18}O + 10$) checking the reliability of the data. Points along a line with smaller steepness than 8 (that of the MWL, see above) and negative d value ($d = \delta D - 8 * \delta^{18}O$) indicate isotopic enrichment of the samples by evaporation (in the field or in the laboratory), therefore these data were discarded.

We could use the isotopic and chemical data about 300 wells for our purpose.
One profile has been chosen for more detailed study of the deep flow pattern, and the relation between the pollution in the surface and shallow groundwater (see Fig. 1).

DISCUSSION

The regional groundwater flow directions determined by hydraulic data are indicated on Fig. 1. The radiocarbon data are in good agreement with this flow system. From the recharge area (central part between the Rivers Danube and Tisza, Fig. 1) to the River Tisza the uncorrected ^{14}C ages vary from 0 to 20-30 thousand years along the flow paths. In the recharge area the uncorrected ^{14}C age increases by depth (e.g. at Jánoshalma (Fig. 2): 70 m - 3500 years; 167 m - 9300 years), while in the discharge area it decreases by depth (e.g. at Mindszent (Fig. 2): 199 m - 26500 years; 480 m - 26000 years). The δD and $\delta^{18}O$ values along the flow path indicated on Fig. 1 and 2 vary from -64 to -95‰ and from -9.3 to -11.9‰ respectively indicating Holocene water in the recharge area and Pleistocene water in the discharge area.
The pollutants in the regional recharge areas infiltrate in a higher rate and reach greater depth than in the discharge area, because the hydraulic perch (upwelling) of the groundwater in the discharge area weakens the downward migration of the pollutants. For this phenomenon a good example is the variation of nitrate content by depth shown in Table 1.

Table 1. Average nitrate content [mg/l] vs. depth in recharge and discharge areas

Depth	Recharge area:	Discharge area:
0-10 m	363	327
10-20 m	55	no data
20-50 m	35	5.6
50-100 m	2.3	no data

The relation between the pollution sources and the distribution of pollutants will be shown in details.

Acknowledgement: The stable isotope measurements of samples taken by the authors were supported by the Hungarian National Scientific and Research Fund (OTKA T014968).

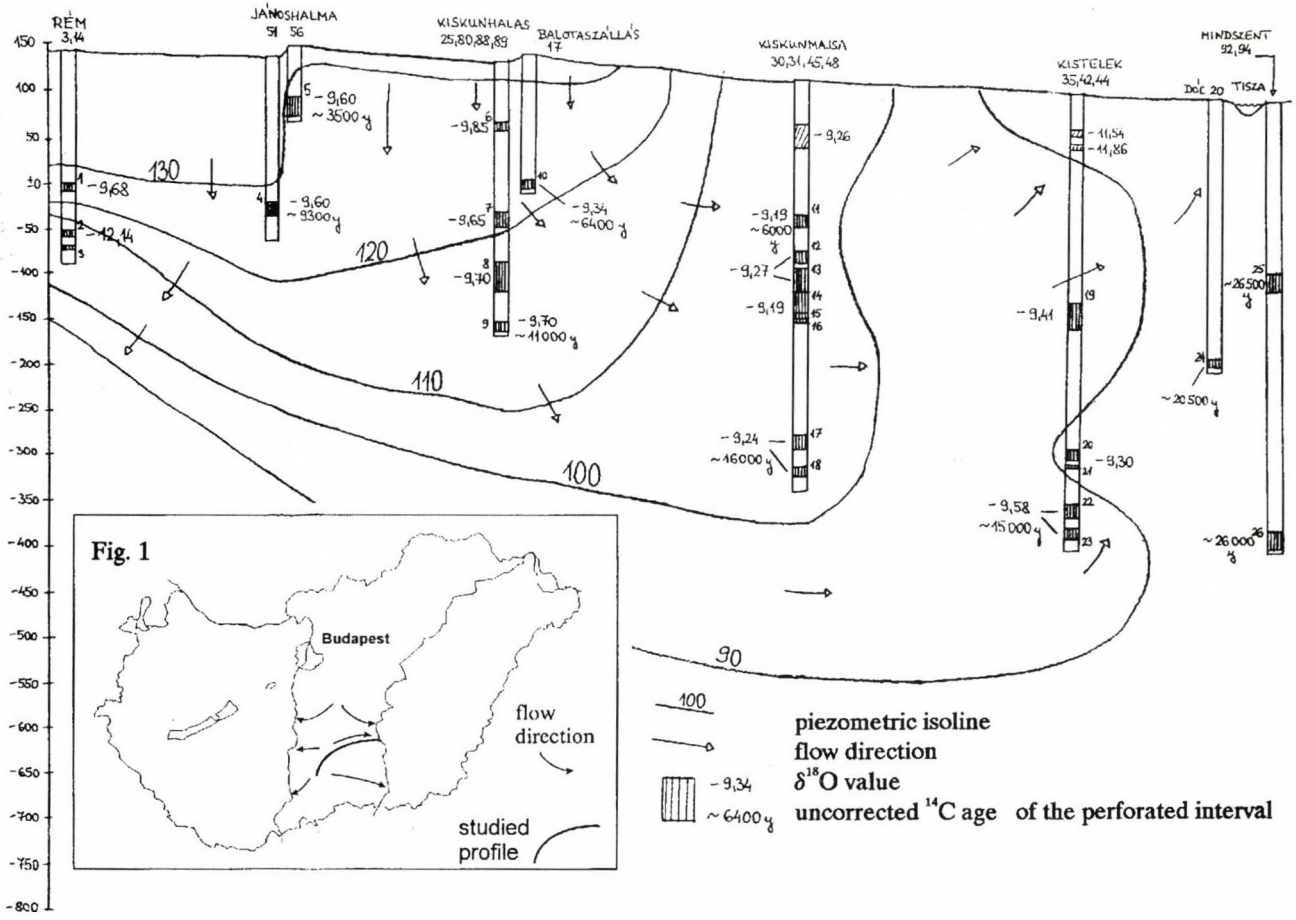

Fig 2. Flow pattern of the profile shown on Fig. 1 with $\delta^{18}O$ values and uncorrected ^{14}C ages

PALEOHYDROLOGICAL FEATURES AT A REGIONAL UNCONFORMITY. SEDIMENTOLOGICAL OBSERVATIONS SUPPORTED BY STABLE ISOTOPE ANALYSES: EXAMPLES FROM THE CRETACEOUS OF CAMPANIA (S. APPENNINES)

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Keywords: paleokarst, stable carbon isotope, Cretaceous, Southern Appennines

Subaerial exposure related to Late Cretaceous emersion of large sectors of the interior of the Apulian plate, resulted in a unique - partly bauxite-filled - paleokarst system exposed at several localities in the Matese-Mte Maggiore area of the Campanian Appennines.

Early syndepositional microkarst features of the shallow water carbonate platform were overprinted and partly destroyed by mature, dm to m scale karstic cavities formed on dissolution of the not yet completely lithified carbonate sediment interacting with descending vadose waters and an extensive fresh-water lens. The establishment of the fresh-water lens was facilitated by the low but dissected subaerial relief formed on exposure of the former shallow water domain.

Extant karst forms include bauxite-filled dolines, medium-depth sinkholes, shallow uvala-type karstic depressions and karren-fields underlain by an intricate system of underground water conduits. Vadose overprinting of pre-existent sedimentary/diagenetic features of the karstified substrate being frequent underneath the unconformities, show that ample quantities of meteoric water percolated through the sediment. Along with the petrographic evidence reequilibration with meteoric waters is shown also by a pronounced ^{12}C-enrichment of the bulk sediment right underneath the unconformity. Sedimentological observations suggest that also the active zone of the unconfined phreatic lens must have been quite extensive (most phreatic cements precipitated from oxidizing or at least intermittently oxidizing solutions). The estimated time-span represented by exposure-related features varies from 2 to 4 million years (from latest Albian Cenomanian to early Senonian).During this time interval underground cavities became only partially filled, and the remaining open space was finally plugged only when rising sea level gradually drowned the former carbonate island. Accordingly in many of the cavity systems a succession of various mechanical and chemical cavity fillings can be observed, recording the story of the formation and choking of the karst porosity from early via late, phreatic to vadose and again phreatic environments, at the end overlapping with the story of the transgression.

That drowning was not only gradual but also differential is shown by intense meteoric lens related dissolution features observed also *above* the regional unconformity at least at those localities which were inundated first. One of the effects of differential subsidence could have been a complex circulation pattern permitting fresh-water influx from the still exposed terraines into the pore space of submerged areas. Depending on the intensity of recharge the chemistry of pore-water is supposed to have been subject to frequent fluctuations producing intense mixing-corrosion related dissolution cavities.

Changes of pore water chemistry suggested by optical petrographic work were checked by cathodoluminescence and by stable isotope analyses of the individual cement phases recognized.

Complex cavity fills consisting of laminated mechanical infill overgrown by several generations of cements (both radiaxial and bladed, brightly luminescent, dull or non-luminescent) were microsampled and analysed separately. $\delta^{13}C$-values changing from -2‰ to +0.67‰ and back to near zero again were interpreted as having been precipitated from pore-waters of mixed composition in which the ratio of fresh to saline water fluctuated. Fluctuations could have been controlled either by sea-level oscillations, or by the effects of intermittent influx of meteoric waters from the vadose zone into the mixing zone of the confined section of the meteoric lens.

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Synthesis of [1,3,7-$^{15}N_3$, 8-^{13}C] Xanthyne

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The synthesis of [^{15}N, ^{13}C] - labelled xanthyne, using $CO(^{15}NH_2)_2$, $Na^{15}NO_2$ and $H^{13}COOH$ as starting isotopically labelled material, is presented.

The experimental procedure is an adaptation of the synthesis methods for the corresponding unlabelled compounds (the Traube method, modified by Bobransky and Synowiedsky was used).

Xanthyne, isotopically labelled with ^{15}N and ^{13}C will be used as starting material to produce some nucleotides by enzymatic synthesis.

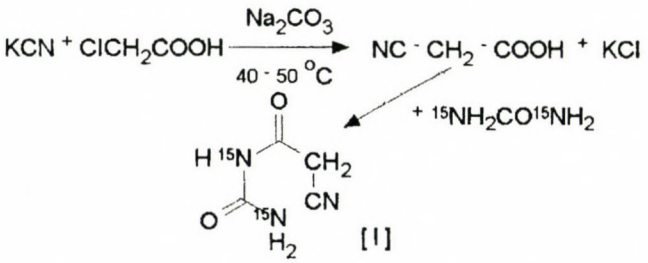
The ^{15}N - labelled compounds used as starting material were obtained from $H^{15}NO_3$ (99 atom % ^{15}N) produced at the Institute of Isotopic and Molecular Technology.

The xanthyne structure was confirmed using the mass spectrometry method and the isotopic label was determined by mass spectrometry on the molecular compound.

Key words: [^{15}N]-xanthyne, [^{13}C]-xanthyne, synthesis, urea-$^{15}N_2$, sodium nitrite-^{15}N, formic acid-^{13}C.

Experimental

1. Synthesis of cyanoacetylurea-(1,3-$^{15}N_2$) [I]
(J.W.Triplett et al., 1978)



[I]

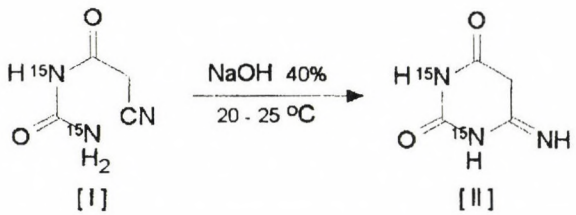
Chloroacetic acid (3.46 g) was dissolved in a minimum amount of water and neutralised by addition of anhydrous sodium carbonate. 1.97 g KCN in 10 ml of water were added to the sodium chloroacetate solution and the temperature allowed to rise to 60 °C.

The reaction continued until the temperature ceased to rise, then the mixture was allowed to stand for twelve hours at room temperature. The resultant pale yellow solution was acidified and the excess of HCN, water and HCl were removed under reduced pressure at 50 °C. The residue was taken up in absolute alcohol and the solvent removed.

A suspension of urea-$^{15}N_2$ (1.86 g) in freshly distilled acetic anhydride was added to the dried residue and the mixture was heated at 100 °C for 30 minutes. Water was then added to the solution and upon cooling a crystalline solid was isolated, that

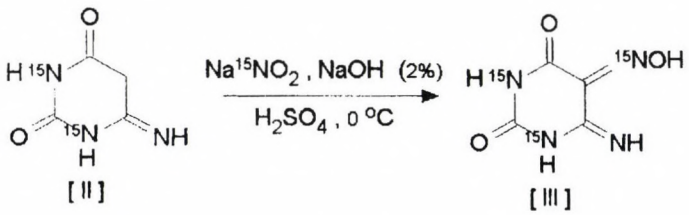
proved to be cyanoacetylurea-1,3-$^{15}N_2$, in 82 % yield relative to urea. The melting point of the product is 211-2 °C.

2. Synthesis of iminobarbituric (1,3-$^{15}N_2$) acid [II]
(B.I.Hmelevski et al., 1958)



The cyclisation of I to II was made with 40 % NaOH solution. The mixture was stirred for 2.5 hours, keeping the temperature at 20 - 25 °C. Then the reaction mixture was neutralised with HCl 1:1 and allowed to stand for twelve hours in a refrigerator. The final product (2.72 g) II was isolated by filtration.

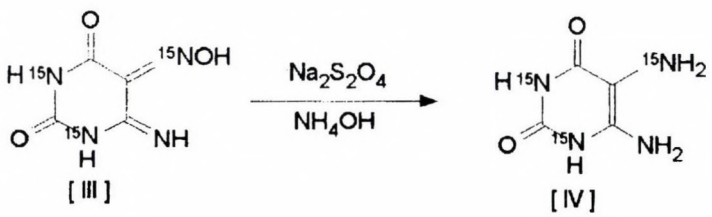
3. Synthesis of iminovioluric (1,3-$^{15}N_2$) acid [III]
(H.Biltzu et al., 1923)



For the nitrosation compound II was dissolved in 2 % NaOH solution and 2.18 g of sodium nitrite-^{15}N were added. The mixture was cooled to 0 °C and conc. H_2SO_4 was added drop wise until the solution became dark violet.

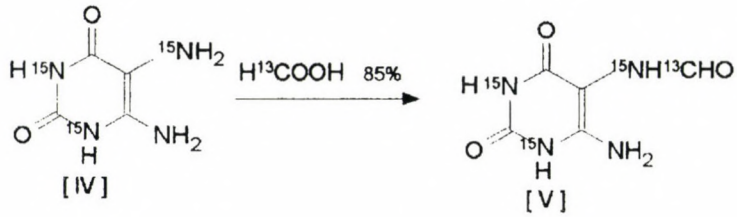
After neutralisation with ammonium solution the red precipitate obtained was isolated by filtration, yielding 3.23 g (84 %).

4. Synthesis of 4,5 - diaminouracil (1,3,7-$^{15}N_3$) [IV]
(B.I.Hmelevski et al., 1958)



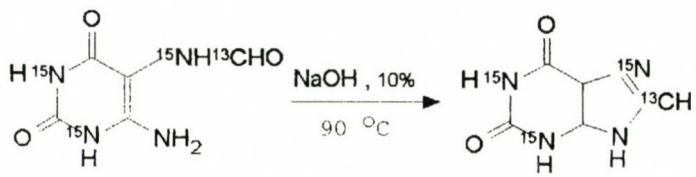
To the suspension of III in water were added 2.4 ml of 19 % ammonium solution and 15.6 sodium hydrosulfide. The mixture was heated to 55 °C until the solution was decoloured entirely. After cooling, the product was filtered and washed with water (the yield was 2.59 g of IV, 96 %)

5. Synthesis of 4-amino, 5-formylaminouracil (1,3,7-$^{15}N_3$, 8-^{13}C) [V]
(B.I.Hmelevski et al., 1958)



To the suspension of IV in 10 ml of water 1.5 ml of formic acid-^{13}C, 85 % were added and the mixture was refluxed for 60 min. Then, the reaction mixture was allowed to stand for twelve hours at room temperature. The product was filtered, washed with water and dried at 60-70 °C, yielding 2.86 g of V (91 %).

6. Synthesis of xanthyne (1,3,7-$^{15}N_3$, 8-^{13}C) [VI]
(W.Traube, 1900)



Compound V was suspended in 10 ml of water and 10 % NaOH wolution was added drop wise up to pH=9. Then, the reaction mixture was heated to 90 °C and kept at this temperature until the solution became clear. After cooling to 0 °C, the solution was neutralised with HCl 1:1 and allowed to stand for twelwe hours in the refrigerator. Then, the product was filtered yielding 2 g of xanthyne (1,3,7-^{15}N, 8-^{13}C) (78 %).

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Isotopes and the development of science (Review paper)

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Since the concept and name "isotope" was introduced by Soddy at the beginning of our century, the isotopes have ever played a prominent role in the development of science. In the first years the mere recognition of their existence helped much to establish the modern atomic and nuclear theory. And after 1913 when Gy. Hevesy (Budapest) initiated the isotope tracer technique, the applications of isotopes (both stable and radioactive) has become a standard practice in all fields of scientific research.

The wide variety of the applications of isotopic tracers can be demonstrated even by the examples collected during the research activity of our small group. Let me mention to you some of them.

In the case of mass spectrometric impurity control of various materials, e.g. high purity gases, it is a prerequisite to have very low level background peaks at the mass numbers of the impurities to be controlled, or at least very stable peaks. Controlling some oxygen-free reagent gases we observed a very small, but variable m = 32 peak. It was necessary to find its origin. By a tiny droplet of water enriched in ^{18}O we have found that O_2 appears in the system by decomposition of H_2O at surface of the cathode in the ion source (Cornides, 1966).

^{18}O tracer was used also to elucidate the kinetics of some reactions in boiling sulphuric acid. (Schulek et al, 1961; Cornides, 1964).

^{15}N isotope was used as tracer to investigate the reason of insufficiency of erythrocites in the blood circulatory system of patients suffering from thermal anaemia. The result was very interesting: in contrast to the expectation on the medical side it was found that the production rate of the red cells is not decreased. We have measured even higher amount of new red cells produced in the same time, than in the case of the healthy control persons. We have measured, however, considerably shorter life span of the erythrocites indicating their much less satisfactory quality. (Cornides et al.,1970). This was a typical biomedical application.

In a quite different field (mining industry) a ^{13}C isotope investigation has made possible to identify the origin of the frequent and very dangerous high energy carbon dioxide outbursts in a coal mine in the Mátra mountain of Hungary, and to design the safety measures accordingly. (Cornides, and Sült, 1970). This result encouraged us to carry out an extensive investigation of the isotope geochemistry of the CO_2 occurrences in the Carpathian Basin. The statistical evaluation of the data obtained indicated mantle origin of the carbon dioxide in this region (Cornides and Kecskés, 1982 and 1987) and this conclusion was strongly supported by helium isotope measurements (Cornides et al., 1986).

Another geological research was carried out to elucidate the formation mechanism of a hydrothermal ore vein by oxygen isotope paleotemperature measurements (Cornides and Kiss, 1976).

We started to apply the isotope tracer technique in the field of cluster chemistry when we had to investigate what kind of Al_xO_y clusters are formed and by which mechanism in the plasma of high energy discharge (plasma technology to produce high purity alumina). By the use of $^{18}0$ tracer we have shown that the oxide species are formed by reactions of single atoms and ions in the plasma (Cornides and Gál 1978), on the other hand a ^{13}C tracer experiment has shown that a not negligible part of the Cn clusters appearing in the discharge between graphite electrodes originate directly from the electrodes as polyatomic fragments of the graphite crystal lattice (Cornides and Morvay, 1992).

Finally, an example from the field of chemical physics. Some years ago we detected in the mass spectra of sulphur the S^2 molecule with three positive charges (Ujpál et al., 1988). The existence of this S_2^{3+} ion was, however heavily disputed in spite of the evidence provided by high accuracy mass measurements. In a second experiment mass spectra of normal sulphur and of sulphur enriched to 94 % in the isotope ^{34}S were taken on the same photoplate. As expected, a second line of 3+ ions was also found in the spectrum shifted from the first one by a distance corresponding exactly to the mass difference of the isotopes ^{32}S and ^{34}S. (Morvay and Cornides, 1992). This evidence was accepted.

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Environmental isotope study of Lake Balaton

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Several boreholes were drilled in order to perform wide-ranging investigations of the lake (Fig. 1). Isotope geochemical tests have proved to be very efficient, allowing us to have a better understanding of some environmental problems of Lake Balaton including rate of sedimentation, physical properties and underwater motion of mud etc. Results contributed further data on the age of Lake Balaton, and it past climate.

Major results:

(1) Around Lake Balaton, peat development started in the beginning of the Postglacial (Bölling), and lasted approx. 1500 years. It was most widespread in the Allerőd.

(2) Oxygen isotope ratios measured on the autochtonous carbonate deposits in the lake and on carbonate shells of gastropods are influenced mainly by the evaporation of water. In addition, the latter indirectly depends on the climatic conditions of the particular region too (Fig. 2). The measured values of oxygen isotope ratios allow us to trace the gradual warming-up in the Holocene.

(3) Most of the carbonate in the lake deposits was formed in-situ. Only a negligible amount was transported from the catchment area.

(4) Comparative analysis of $\delta^{18}O$ trends in lake water and the weather conditions shows that, due to intensive evaporation, the oxygen isotope ratio of the water in Lake Balaton is close to that of sea-water and considerably differs from the values for rivers and meteoric water in Hungary. In Hungary, the average $\delta^{18}O$ value is -9.5 %. for meteoric water, relative to seawater. In the oxygen isotope ratio of the water of Lake Balaton seasonal changes can be well observed (Fig. 3).

(5) A part of the organic matter included in the mud of the lake originates from the recycling of the biological carbon. This process has been going on since the formation of the lake which implies a relative enrichment in ^{12}C (Fig. 4).

(6) Artificial radio-isotope contamination entering the atmosphere since 1950 can be well traced in the mud of the lake (Fig. 5). The location of peaks has allowed us to determine the rate of sedimentation. Under undisturbed hydrological conditions, this value ranges form 0.5 cm/year to 1.4 cm/year. The rate of sedimentation changes by time, and in recent years, it has showed a dramatic increase to 2 to 6 cm/year. At some points of Lake Balaton there is underwater sediment transport and accumulation. As shown by our measurements the top 2 to 3 cm of the mud is disturbed by the storms over the lake.

Reference

T. Cserny, E. Hertelendi, S. Tarján: Isotope-geochemical studies and their results in the gological investigations of Lake Balaton. *Acta Geol. Hung.*, in press.

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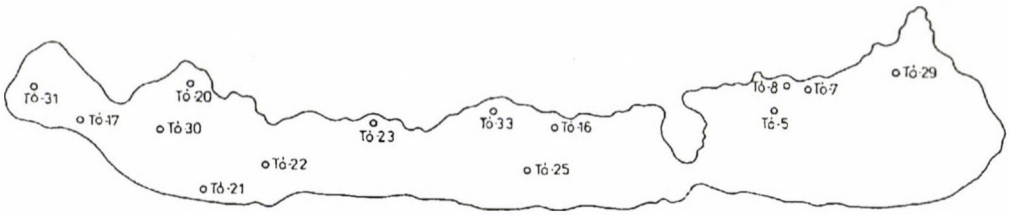


Fig.1. A layout of boreholes and sampling sites

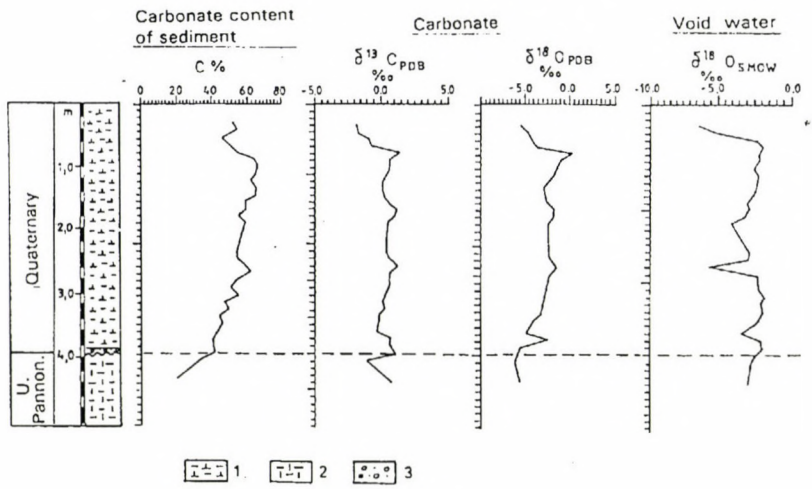


Fig.2. The $\delta^{13}C$ and $\delta^{18}O$ values, vs depth, measured in samples from borehole Tó-25

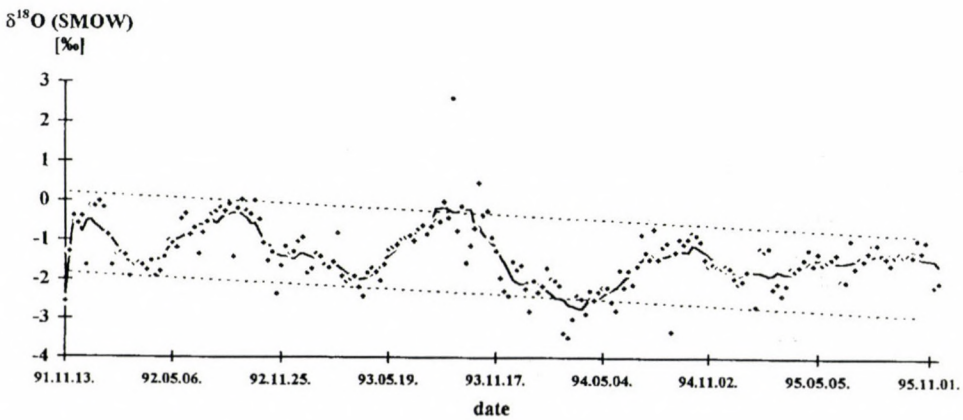


Fig.3. The $\delta^{18}O$ value of the water of Lake Balaton during 1991-1995.

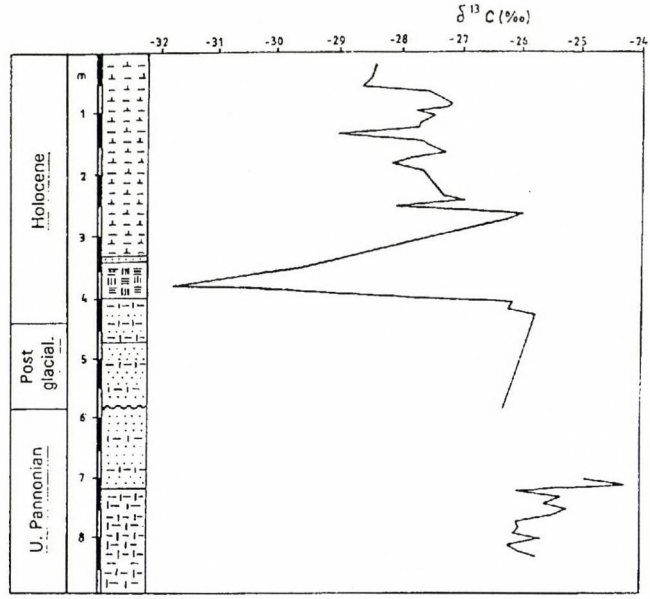
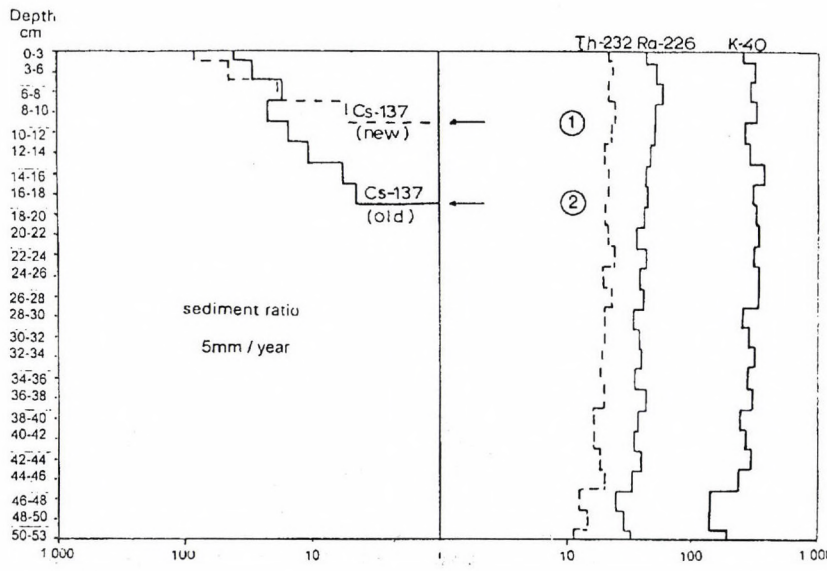


Fig.4. The variation of $\delta^{13}C$ value vs depth, in the organic matter taken from borehole Tó-31



A stable isotope study on the evolution of Canary Island carbonatites

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Keywords: stable isotopes, carbonatites, Canary Islands

Fuerteventura - the second largest of the Canary Islands - contains two main geological units: the Basal Complex (submarine volcanics and plutonic rocks) and a younger volcanic series consisting mainly of lava flows and dikes. Beside basaltic dikes and ultramafic plutonics, the Basal Complex contains two carbonatite-ijolite-syenite intrusive complexes (Ajui-Solapa and Esquinzo). Although stable oxygen and hydrogen isotope studies on silicate rocks (Javoy et al., 1986) indicate interactions with meteoric waters, combined radiogenic and stable isotope studies on carbonatites (Hoernle and Tilton, 1991) showed no influence of crustal contamination or water-rock interaction. However, the structures of the carbonatites suggested the presence of fluid influence, thus we determined stable carbon and oxygen isotopic compositions of a new collection on carbonatites (see figure).

From the isotopic distributions the following conclusions can be drawn:

- most of the carbonatites fall within primary $\delta^{13}C$ and $\delta^{18}O$ ranges. The most primitive compositions can be estimated at $\delta^{13}C$=-6.4 ‰, $\delta^{18}O$=6.2 ‰.
- coupled positive $\delta^{13}C$ and $\delta^{18}O$ shifts appear in the Ajui-Solapa complex that can be attributed to magmatic fractionation processes.
- interactions with external, low-$\delta^{18}O$ fluids (of meteoric or seawater origin) caused negative $\delta^{18}O$ and positive $\delta^{13}C$ shifts in the carbonatites.

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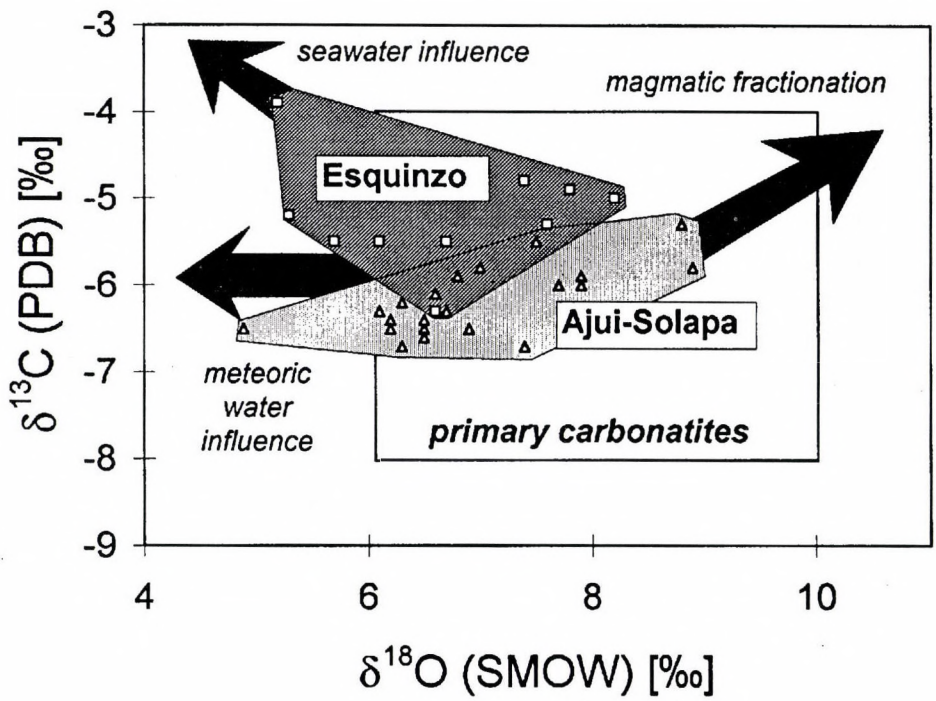

Fig. 1. Stable carbon and oxygen isotopic compositions of two carbonatite complexes of Fuerteventura, Canary Islands, Spain

Investigations on the role of Mg-metasomatism and metamorphic conditions during the formation of Mg-chlorite-muscovite-quartz-phyllites ("leucophyllites") of lower austroalpine nappes of the Eastern Alps (W. Hungary) and Alpine whiteschists

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Keywords: leucophyllite, whiteschist, Alps, Mg-metasomatism, stable isotopes, geothermometry, fluid sources

Mg-chlorite-muscovite-quartzphyllites ("leucophyllites", Starkl, 1883) and Mg-chlorite-kyanite-quartzites were formed in the Sopron-Fertőrákos gneiss-micaschist complex of Western Hungary during an upper Cretaceous metamorphic event (Vendel, 1972, Moreau, 1981, Kiesl et al., 1983, Kisházi and Ivancsics, 1986, Prochaska, 1985). The metamorphic influence caused breakdown of feldspars and biotite and produced newly formed phengite in the precursor granitic rocks. Formation of "leucophyllites" took place in shear zones and was associated with depletion in alkalies and iron and enrichment of MgO and H_2O. Similar chemical and mineralogical changes have been observed in micaschist - kyanite-quartzite transitions. Based on Si p.f.u. values of phengites (up to 3.34) and on stability conditions of the Mg-chlorite+quartz assemble (Massone and Schreyer, 1989), the metamorphic pressure is estimated at 10-12 kbar at 530-550 °C. Fe-depletion and Mg-enrichment at the margins of relict igneous muscovites and in newly formed phengites of "leucophyllites" suggest Mg-

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metasomatism during the metamorphic event. The same conclusion is drawn from whole rock chemical data. Mg-enrichment relative to the precursor granitic rock has been observed not only in "leucophyllites", but also in sheared gneisses, indicating movements of Mg-rich fluids. An extreme end of the metasomatic process is represented by a leuchtenbergite phyllite that consists of >95 % Mg-chlorite.

Material gains and losses have been determined using isocon diagrams and composition-volume relationship calculations (Grant, 1986). Proceeding from metagranite through transition rocks to "leucophyllites", MgO, H_2O, FeO, and alkalies show *continuously* increasing dispersion in isocon plots. The kyanite-quartzites fit well in this isocon plot series. No significant mass and volume change occurred during "leucophyllite" formation, although the relative MgO gain (related to Al_2O_3) increases to 7.35. Abrupt changes appear in the leuchtenbergite phyllite where mass and volume losses of 31 and 41 %, respectively, are associated with a relative MgO gain of 54.7.

Visual assessments of isocon diagrams and composition-volume relationship calculations suggest genetic links between the "leucophyllites" and Alpine whiteschists. The geochemical characteristics of the Dora Maira whiteschists (Italy) and their country gneisses (Tilton et al., 1991) are very similar to those of the Sopron "leucophyllites" and kyanite-quartzites, supporting the theory of Mg-metasomatism responsible for the unusual whiteschist chemistry. The whiteschists of the Adula nappe (Switzerland) are surrounded by eclogites and micaschists (Santini, 1991). Continuous gradation from eclogite to whiteschist indicate that the eclogite could have been the precursor that suffered metasomatism.The results of isocon plotting and composition-volume relationship calculations further support this conclusion.

Based on oxygen isotopic compositions of relict igneous muscovites, the precursor granitic rock had a $\delta^{18}O$ value around 13 ‰ proving its crustal anatectic origin. The formation of "leucophyllites" was associated with ^{18}O-depletion resulting in whole rock compositions around

8.5 ‰ (calculated from mineral separate data). Quartz-mineral oxygen isotope fractionations yield a metamorphic temperature of 550 ±20 °C that is in excellent agreement with earlier estimations based on mineral stabilities (Vendel, 1972, Moreau, 1981).

H isotopic compositions of chlorite+muscovite mixture samples of "leucophyllites" range from -40 to -35 ‰ showing correlations with chlorite amounts. The chlorite and muscovite components have δD values around -30 and -40 ‰, respectively. Agreements between H isotopic compositions of white micas of "leucophyllites", gneisses and metagranites suggest an overall equilibration with respect to H isotopes. Fluid compositions can be assessed from chlorite data, yielding a H isotopic composition around 0 ‰. This composition suggests a seawater origin for the metamorphic fluids responsible for the Mg-metasomatism. A similar conclusion has been drawn by Sharp et al. (1993) for the Dora Maira whiteschists (W. Alps, Italy).

The fluids in equilibrium with "leucophyllites" had oxygen isotopic compositions around 7.8 ‰, that agrees well with that calculated for the Dora Maira whiteschists (7.6 ‰), supporting the assumption of "leucophyllite"-whiteschist relationship. Regarding the similarities in the formation processes presumed for these rocks, their formation can be attributed to metasomatism by Mg-rich fluids during the eoalpine subduction-related metamorphic phase. A possible source of these fluids is found in the mafic-ultramafic complex of the Penninic ocean crust, whose subduction might have brought significant amounts of fluids (partly as pore waters that retained the original seawater H isotopic composition) to mantle depths during the upper Cretaceous. The accordance between oxygen isotopic compositions of metasomatic fluids (7.6 to 7.8 ‰) and serpentinites of the Central Alps (7.1 ‰ on average, Burkhard and O'Neil, 1988, Früh-Green, et al., 1990) further support this assumption.

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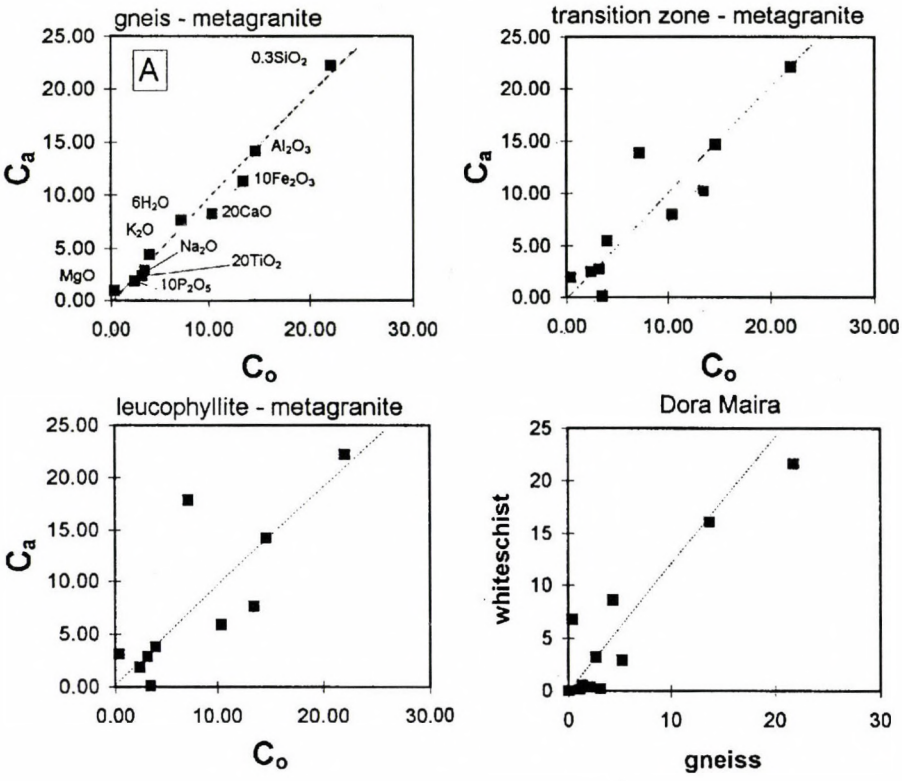

Fig. 1. Isocon diagrams of selected elements (Grant, 1986) of the gneiss-"leucophyllite" asemblage of the Sopron Mts. (W. Hungary) and of the Dora Maira whiteschist (chemical compositions from Tilton et al., 1991). Dashed lines connect origins and Al_2O_3 data points.

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Groundwater Origin and Dating Studies in Szigetköz

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The aim of the isotope hydrological study was to determine the origin and rate of movement of ground water in the thick gravel aquifer in the Szigetköz region. The isotope hydrological data can be used for verification of hydraulic models developed for describing the ground water movement of the area too. The isotope distribution simulated by the hydraulic models should be compared with the measured isotope values.

There are different potential sources of the groud water in the gravel aquifer: (1) upward leakage of Pliocene ground water from underlying aquifers, (2) downward infiltration of local precipitation, (3) horizontal leakage of Danube River water.

The order of ground water ages was determined by ^{14}C dating as the first step of the study. The ages of ground water in the gravel aquifer were very young (<2-3 thousand years) in the Szigetköz region. In contrast with this very old (20-30 thousand years) ground waters were found in the underlying Pliocene aquifer. It means that the leakage rate of the old Pliocene ground water is negligable in the recharge of the gravel aquifer, only a small amount of it can be detected in the bottom of the gravel aquifer.

Theoretical background of the use of the stable oxygen isotope ratios ($\delta^{18}O$) is the natural tracing. It means, that the original $\delta^{18}O$ of the ground water does not change through subsurface flow and is useable to characterize the conditions of infiltration.

The ratio of ground water originating from the Danube to the locally infiltrated water was calculated by the isotope dilution, using the fact, that $\delta^{18}O$ of Danube water (Fig. 1/d) is significantly different from the $\delta^{18}O$ of locally infiltrated ground water (Fig. 1/a).

The average $\delta^{18}O$ content (-11.1 ± 0.4 ‰) of the shallow ground water in Szigetköz region (Fig. 1/e) is significantly diffent from the $\delta^{18}O$ of the shallow ground waters of the other regions of Hungary (-9.3 ± 0.4 ‰ ; see Fig. 1/a). The ratio of Danube water in shallow ground water can be calculated as 80 - 100 % in northern and 50 % in southern part of the Szigetköz.

The isolines of Danube-water ratio in the shallow ground water drawn by $\delta^{18}O$ data (Fig. 2.) show that the ground water originated from the Danube is dominant in area West to Szigetköz, and North to Lajta River too. At greater distances the ratio of Danube water decreases rapidly, at Rábca River it is only 20 %. South and West from the Rábca River the -9 - -10 ‰ $\delta^{18}O$ values are found, which are similar to the other areas of Hungary, and mean 0 -20 % Danube water ratio. There are two areas where horizontal recharge from Austria can be supposed (Fig. 2.).

The screens of deeper (>20 m) ground waters are variable, so isolines of $\delta^{18}O$ can not be constucted. By the average $\delta^{18}O$ of deep ground water (-11.3 ± 0.3‰) 90 ± 10 % Danube water ratio can be calculated (Fig. 1/f).

Tritium (^{3}H) is the ideal tracer of water as like as ^{18}O. Detectable tritium concentration (>1 TU) can be found only in ground waters infiltrated after 1952. The Danube water intensively outflush the whole gravel aquifer, because we could find detectable tritium even in the deeper wells in the gravel. This very fast flow means that this gravel aquifer is extermly vulnerable.

The tritium peak in precipitation of 1963 was measured in Danube water too, so the ground water seeped from the Danube in 1963 can be characterized with anomaliously high tritium content nowadays too. The distance of the tritium peak in the ground water from Danube is used for calculation of the subsurface flow velocity as 400-500 m/y in aquifer of depth 60 - 100 m. Along the flowpath of Dunakiliti - Mosonmagyaróvár - Öttevény (Fig. 2.) 475 m/y ground water flow velocity was calculted by the tritium peak method (Fig. 3.). Using the more precise tritium/^{3}He dating method along the same flowpath the ground water flow velocity was 600 m/y.

The freons can be found in environment by human origin, and their concentration is monotonously increasing in precipitation. Investigating the freon content in ground water along the flowpath in Fig. 2. surprisingly high, (even higher than recent precipitation) concentrations were measured. The freons are conservative tracers, so they can not accumulate in the ground water. The most probable source of the high freon content in ground water looks be the Danube water have been polluted by freon by the untreated sewage water of Vienna and Bratislava.

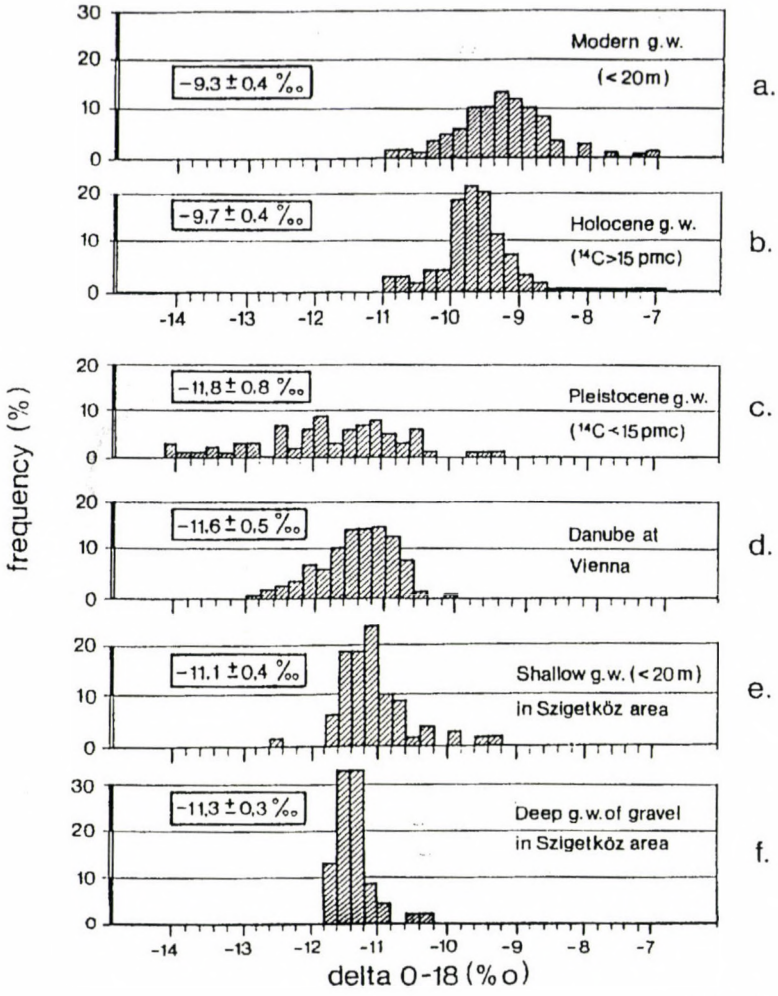
frequency (%)
-9,3 ± 0,4 ‰
Modern g.w.
(< 20m)
a.
-9,7 ± 0,4 ‰
Holocene g.w.
(14C>15 pmc)
b.
-11,8 ± 0,8 ‰
Pleistocene g.w.
(14C<15 pmc)
c.
-11,6 ± 0,5 ‰
Danube at
Vienna
d.
-11,1 ± 0,4 ‰
Shallow g.w. (< 20 m)
in Szigetköz area
e.
-11,3 ± 0,3 ‰
Deep g.w. of gravel
in Szigetköz area
f.
delta O-18 (‰)

Fig. 1

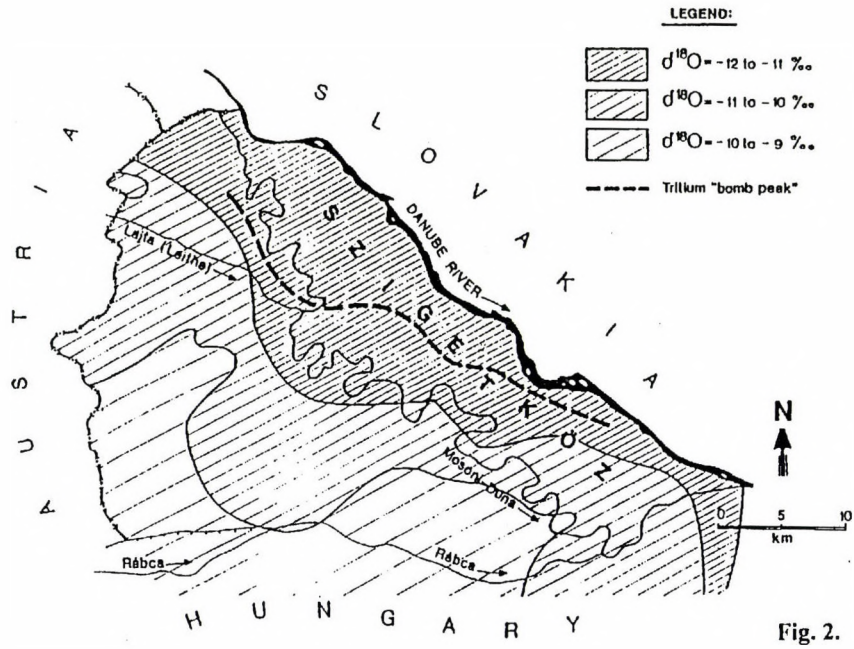
LEGEND:
d18O = -12 to -11 ‰
d18O = -11 to -10 ‰
d18O = -10 to -9 ‰
Tritium "bomb peak"
AUSTRIA
SLOVAKIA
HUNGARY
DANUBE RIVER
Lajta (Leitha)
Rábca
Mosoni-Duna
N
0
5
10
km

Fig. 2.

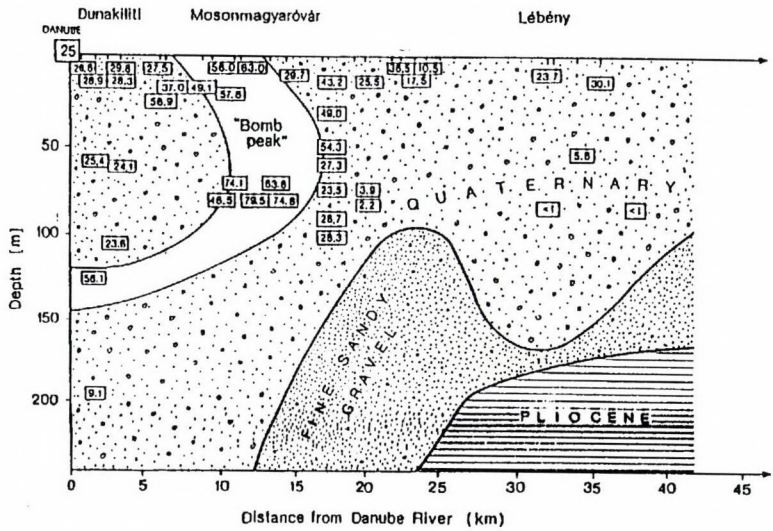
Dunakiliti
Mosonmagyaróvár
Lébény
DANUBE
"Bomb peak"
QUATERNARY
FINE SANDY GRAVEL
PLIOCENE
Depth [m]
Distance from Danube River (km)

Fig. 3.

Stable isotope study of the Adriatic Sea

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Keywords: Adriatic Sea, stable isotopes, fresh water effects

ABSTRACT

The Adriatic as a marginal and semi-enclosed sea is generally enriched in heavy oxygen and hydrogen isotopes. The variations of $\delta^{18}O$ and δD are in the range from about - 1.96 to + 1.49 ‰ and from - 20,1 to + 8.1 ‰. In surface water these variations could be satisfactorily explained in terms of the seasonally variable isotopic composition of local riverine inflows, precipitations and evaporation effects. Isotope depth profiles also revealed the different origins of water masses. In the central Adriatic at depth between 40 and 140 m isotopically heavy saline water with $\delta^{18}O$ values between + 1.25 and + 1.36‰ may be related to the ingression of isotopically heavy water from the east Mediterranean.

INTRODUCTION

The aim of this study was to get the general insight in circulation and distribution of the water masses in the Adriatic Sea as well as their contaminations with riverine inflows.

MATERIALS AND METHODS

Seawater samples were collected along the eastern Adriatic coast and in the open Adriatic, while riverine and brackish water were sampled in the rivers, stream and estuaries along the Slovenian, Croatian and Montenegro coast. All surface water samples were collected in polyethylene bottles, while the water column was sampled using Nisken bottles. Riverine, brackish and seawater samples were prepared for $\delta^{18}O$ measurements according to the standard CO_2-water equilibration method (Epstein and Mayeda, 1953). Deuterium content of riverine water was measured in hydrogen gas obtained from water passed over zinc at 450°C (Riedman, 1953), while the determination of the deuterium content in brackish and seawater was followed the recommendations of Gat (1979) and Sofer and Gat (1972; 1975). The isotopic analyses were performed on a Varian MAT-250 isotopic ratio mass spectrometer. The $\delta^{18}O$ and δD values were reported in standard per mill (‰) notations relative to SMOW standard. The analytical reproducibility for $\delta^{18}O$ and δD is $\pm$ 0.1 and $\pm$ 2 ‰.

RESULTS AND DISCUSSION

The isotopic composition of Adriatic waters is not homogenous either horizontally or vertically, and shows considerable seasonal variations. Since the northern Adriatic is the source of low salinity water due to the inflow of river Po and other Italian as well as Slovenian rivers, it is also

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enriched in light oxygen and hydrogen isotopes. The effects of fresh water inputs are usually more expressed along the W (Italian) coast, while along the E (Slovenian, Croatian and Montenegro) coast they are felt only to a lesser degree.

In the southern part of the Gulf of Trieste (northern Adriatic) the seasonal variations of $\delta^{18}O$ and δD values of surface water ranged from - 1.96 to + 1.49 ‰ and from - 20.1 to + 7.6 ‰. These values differ from those of bottom waters which are slightly enriched with heavy oxygen (from + 0.54 to + 1.49 ‰) and hydrogen isotopes (from + 3.2 to + 8.1 ‰). The $\delta^{18}O$ and δD of ocean water are usually close to zero and vary only within a narrow range. A mean $\delta^{18}O$ for ocean surface waters was estimated by Craig (1965) at + 0.5 ‰. The Mediterranean and Adriatic Sea as semi-enclosed basins are due to excess evaporation slightly enriched in ^{18}O and D relative to the ocean water. This enrichment is observed even in the northern Adriatic where the seawater is generally depleted in ^{18}O and D due to the fresh water dilution. The gradual shift of $\delta^{18}O$ and δD from positive to negative values (up to - 4.80 ‰ for $\delta^{18}O$ and up to - 35.5 ‰ for δD) was observed in surface water close to the inflow points of the Rižana and Dragonja rivers.

The isotopic composition of surface waters from the central Adriatic is higher relative to the northern Adriatic. Their $\delta^{18}O$ is generally in the range between - 0.95 to + 1.34 ‰. However, in the coastal area in the vicinity of the mouth of Neretva, Cetina and Krka rivers, where brackish conditions are established, the $\delta^{18}O$ of surface water ranges from - 5.05 to + 0.08 ‰. The fresh water effect on salinity and isotope composition is observed in wider areas throughout the eastern (Dalmatian) coast. The influence of the Neretva river with $\delta^{18}O$ of about - 8.2 ‰ is still felt in the area of Makarska ($\delta^{18}O$ of surface water = + 0.08) which is about 50 km north of the Neretva estuary. The effect of the Cetina river is also observed about 20 km north from the inflow ($\delta^{18}O$ of surface water = + 0.68 ‰). The lowest values were as expected measured in the Krka estuary in Šibenik Bay ($\delta^{18}O$ in surface water - 5.05; in bottom water at - 30 m + 0.90 ‰). The effect of fresh water inflow through numerous springs is also remarkable. In Pirovac Bay where the slightly brackish environment is a consequence of fresh water supply from Vrana Lake through an artificial channel, as well as through numerous submarine spring, the $\delta^{18}O$ values of surface water range between - 2.05 to + 0.60 ‰.

The oxygen isotopic variation of the open surface water from the central Adriatic is less pronounced. In most cases the $\delta^{18}O$ values range between + 1.13 to 1.34 ‰. The shift of $\delta^{18}O$ to lower values just below the surface indicate the evaporation effect on the isotopic composition of the surface water. In vertical profiles from the Jabuka Pit and the Palagruža sill the water column is concerning the oxygen isotope data divided into three layers (Fig. 1): subsurface, intermediate and bottom. The water in the approximately 40 m thick subsurface layer is influenced by riverine inputs and exhibits low $\delta^{18}O$ values ($\delta^{18}O$ ranges from +1.11 to + 1.23 ‰) relative to the intermedicate layer. The later, occupying a depth between 40 and 150 m, is characterized by highly saline water probably originating from the eastern Mediterranean. This Levantine water exhibits $\delta^{18}O$ in the range from + 1.25 to + 1.36 ‰ and a salinity between 38.70 and 38.84 ‰. Isotopically heavy waters with $\delta^{18}O$ ranging between + 1.5 and + 1.6 ‰ have been also found in the central and eastern Mediterranean (Pierre et al., 1986; Steni and Longinelli, 1990). The water masses of the deepest layer in the central Adriatic originate from the northern Adriatic in the wintertime when the surface water reaches sufficiently high density due to extensive evaporation produced by the strong NE wind, called burja (Zore-Armanda, 1963). This high density and cold water spreads towards the central Adriatic filling the deepest part of the Jabuka Pit. In general the lower part of this layer has relatively constant $\delta^{18}O$ of about + 1.29 ‰ and a low temperature varying in a narrow range between 9 and 11 °C, while the upper part is about 3 °C warmer and enriched with the light oxygen isotope ($\delta^{18}O$ range from + 1.12 to + 1.16 ‰).

The $\delta^{18}O$ values of surface water in the southern Adriatic basin along the eastern coast between Dubrovnik and Ulcinj varied from + 0.72 to + 1.06 ‰. These relatively low values are due to the influence of Albanian riverine inflows. A similar oxygen isotopic composition ($\delta^{18}O$ = + 1.07 ‰) was also reported for the seawater south of Bari (Coteccia et al., 1974). In the central part of this basin surface water exhibits $\delta^{18}O$ values close to + 1.29 ‰ which are similar to those from the central Adriatic.

CONCLUSIONS

The variability of oxygen and hydrogen isotope composition of the Adriatic surface waters can be explained by the seasonally variable inputs of local riverine dischanges and precipitations, as well as by variations in balance. Deep water $\delta^{18}O$ record reveals three isotopically different water layers: a 40 m thick subsurface layer consisting of water masses influenced by riverine inputs influenced by evaporation at the surface; an intermediate layer at depth between 40 and 150 m which could be related to the ingression of the Levantine intermediate water from the eastern Mediterranean, and the bottom layer characterized by cold water slightly depleted in ^{18}O originating in the northern Adriatic in the wintertime.

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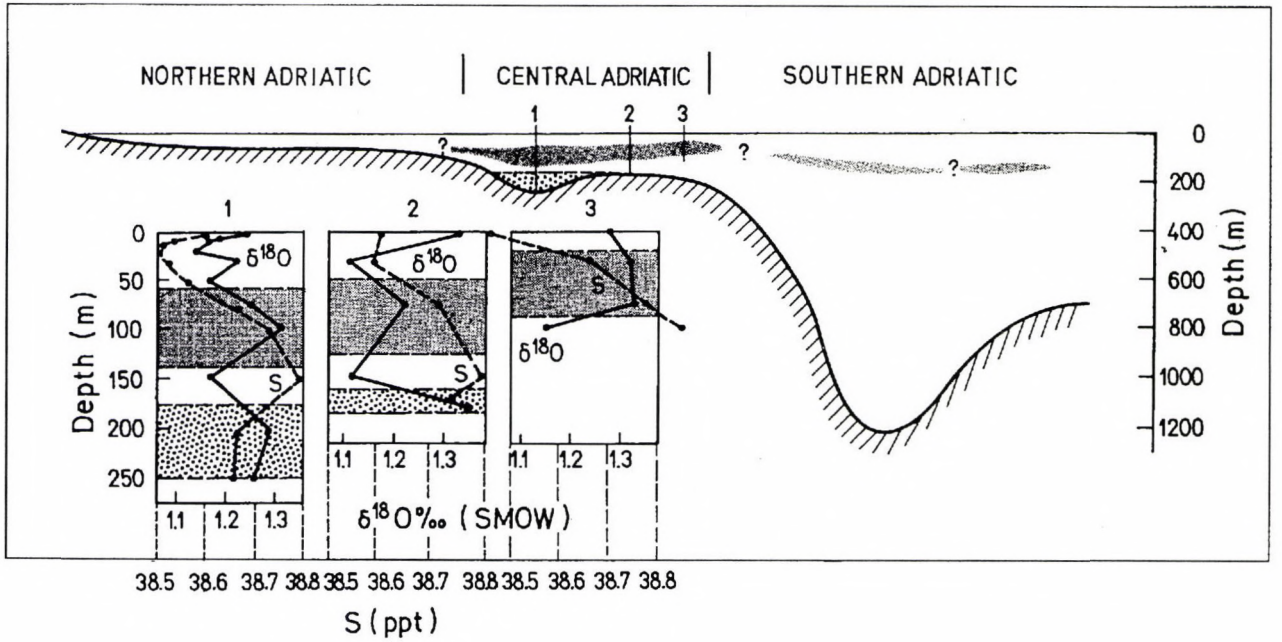
Figure caption

Fig 1. Axial profile of the Adriatic Sea with oxygen isotopic composition ($\delta^{18}O$) and salinity (S) distribution in the central Adriatic: Jabuka Pit (1) and Palagruža Sill (2,3).


NORTHERN ADRIATIC
CENTRAL ADRIATIC
SOUTHERN ADRIATIC
1
2
3
?
?
?
0
200
400
600
800
1000
1200
Depth (m)
1
2
3
0
50
100
150
200
250
Depth (m)
δ18O
S
δ18O
S
S
δ18O
1.1
1.2
1.3
1.1
1.2
1.3
1.1
1.2
1.3
δ18O‰ (SMOW)
38.5
38.6
38.7
38.8
38.5
38.6
38.7
38.8
38.5
38.6
38.7
38.8
S (ppt)

Some Developments in the Ar Extraction and Purification UHV Line

Tomasz Durakiewicz[1]

keywords : K-Ar, $^{40}Ar/^{39}Ar$, crucible, vacuummeter, cold-finger, stabilization

Introduction

The interest in dating methods based on the potassium decay is increasing rapidly nowadays. It is so mostly due to the swift progress in analytical techniques, namely laser extraction (York *et al.* 1981), fabrication of precise solid spikes (Lampert *et al.* 1994) or even new method of argon release by dissolution of the sample in hot HCl (Wampler 1994). These new techniques, as well as the growing experience in understanding the argon dating results, diffuse gradually over the world, being now available to large number of scientists.

The below described devices, namely double-vacuum furnace, cold fingers and Pirani vacuummeter, are parts of the UHV line for argon extraction and purification. Construction of the devices, as well as the operating principles, were adapted in the years 1990 - 1995 to fulfil the needs of dating quality.

Argon extraction and purification line

The process of argon extraction and purification, prior to mass-spectrometrical determination of isotope ratios, is performed in three steps : (1) extraction of argon by melting the sample in high temperature furnace, (2) purification of the extracted gas mixture by freezing of condensable gases on glass surface and (3) purification by Cu_2O and Ti furnaces, and finally by getter. The UHV line is presented in Fig. 1. The detailed description of the line may be found in Hałas *et al.* (1994).

The crucible

Extraction of argon by melting the sample in a crucible under vacuum is still used in the majority of laboratories, mostly due to its simplicity. In some cases, like very young or fine-grained samples, it seems to be the only suitable method. Single-vacuum crucibles and either the resistive or inductive heating are commonly applied in such cases.

Every investigator meets the following difficulties when using this method : (1) the need of handling the thermocouple feedback if the temperature is to be controlled (2) the controllers of the inductive heaters occupy large space and consume a lot of energy; (3) glass-made reactor and intense water cooling are necessary if the inductive heating is used, what substantially increases the waste of energy, (4) large inductivities and interference of electromagnetic fields may produce instabilities in the mass spectrometer signal. Improved design of the reactor and the novel temperature controller has solved all the problems listed above.

The design of our crucible (Fig. 2) is based on the double-vacuum device described by Staudacher *et al.* (1979). It allows to perform continuous melting of samples in temperatures exceeding 1500°C and degasation of the chamber at 1600°C. The hermetic crucible is surrounded by a large-size stainless-steel vacuum chamber. The heater, made of the tantalum wire (O.D. = 1 mm), is placed in the outer vacuum outside the crucible. The outer vacuum is conditioned by the ion pump PZK-20 with pumping speed 20 L/s. The heater is coated by 5 mm of yttria stabilised ZrO_2 ceramic cup. The crucible itself is made of a tantalum cup (O.D.

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20 mm, height 35 mm, wall thickness 0.5 mm) which is welded by means of electron beam with a titanium tube (O.D. 20 mm, height 50 mm). Both materials used, titanium and tantalum, have a high absorption rate for residual gases, which allows to start the purification of argon during extraction. The upper part of the titanium tube is formed as a rotable flange CF19 the stainless steel ring of which is connected to the upper part of the vacuum chamber. The cooling mantle surrounds this part. The glass part of the remaining UHV line is connected to the upper body of the chamber. The temperature of the bottom of the crucible is determined pyrometrically by its observation through a flat Pyrex window located above the crucible. Such a calibration of the temperature controller (described below) is performed once upon a few months.

The temperature controller comprises a Hałas-Kaminski bridge (Hałas and Kamiński 1992, Hałas *et al.*, 1993), a monostable multivibrator, and a zero-cross switchable rectifier, being supplied from separate sources. The measured temperature variations over one working day did not exceed 20 K at 1000 K. Based on the same principle, but low-power varieties of the controller are used in the Pirani vaccuummeter (Durakiewicz and Hałas, 1995) and in the cold fingers controller (Hałas and Durakiewicz, 1995). The detailed description of the electronic circuit is given elsewhere (Durakiewicz and Hałas 1996a, Durakiewicz and Hałas 1996b).

The main advantages of our improved arrangement are : (1) temperature stabilization without thermocouple feedback, only two vacuum feedthroughs are required, (2) low power consumption and small size of the controller, (3) no intense water cooling, (4) purification of argon starts inside of the crucible due to high absorption of gases by tantalum and titanium, (5) no noise is produced in the power supply network.

The Pirani gauge controller

A typical Pirani gauge is used for pressure measurements ranging from 10^{-3} to 1 mbar. The measurement precision is pretty poor at the ends of this range because the heat transfer through the gas becomes meaningless. Some rather complicated gauges, using natural or forced convection have been constructed in order to extend the range of measured pressures up to 1 bar.

The commercial Pirani gauge with PtRh wire was incorporated into the H-K bridge (Durakiewicz and Hałas, 1995). The gauge comprises two such wires, the first of them used for pressure measurements and the second for temperature stabilization of the gauge walls. The H-K bridge controls and stabilizes the temperature of the internal wire. The mean free path of the gas molecules governs the cooling properties of gas. When the mean free path is longer (and the pressure is lower), the heat flow form the hot wire to the walls of the gauge drops down, which means that less power has to be dissipated by the wire to keep its temperature constant. Therefore, the power supplied by the power regulator (in order to keep the temperature of the wire constant) is a measure of pressure.

As every thermal-conductivity vacuummeter, our approach gives different readings for different gases at the same pressure because the thermal conductivity depends on the gas species. The sensitive range of pressure measurements is extended to 10^{2} mbar, which is a very beneficial range in argon extraction and purification procedure.

The adsorbant trap for gases

Trapping of gases by means of charcoal cooled by liquid air is frequently applied in the mass spectrometrical analysis of gases, as well as in argon purification procedure. Only He and Ne are not trapped on charcoal if liquid air (≈80K) is used as a cryogenic medium. All the gases can be trapped by use of liquid He (4.2K). Trapping is usually achieved by use of a so-called "cold finger" which is a sealed glass tube filled with charcoal and connected vertically to the

extraction-purification vacuum line. The main drawbacks of such approach are : (1) external heater must be taken off every time before its cooling with liquid air, (2) waste of time due to slow heat transport to the axis of the cold finger filling and (3) waste of power because the oven is turned on continuously. The simple solution presented in Fig. 3. relies on the permanently installed coil which has a small heat capacity and which is automatically switched off by a simple circuit of our design when immersed in liquid air. Moreover, improved design of the cold finger construction assures a fast access of heat produced by the heating coil not only outside, but also inside the tube. In our tests we adsorbed air at pressure $7 \cdot 10^{-2}$ mbar. Pressure after adsorption fell below 10^{-4} mbar. Time of desorption for the finger of our construction was shorter than for the typical one by a factor of 2.8, whereas the adsorption time was diminished by a factor of 1.5.

The temperature controller was constructed on the basis of the Hałas-Kamiński bridge with reversed input polarity of the bridge signal amplifier. The power, being normally on, is turned off immediately after any drop in the heating coil resistance, e.g. after immersing the finger in liquid air. Power is automatically turned on when the temperature of the coil crosses the selected value.

The comparison of adsorption-desorption properties of both types traps was performed with air under pressure of $7 \cdot 10^{-2}$ mbar. Pressure after adsorption fell below 10^{-4} mbar. Time of desorption for the finger of our construction was shorter than for the typical one by a factor of 2.8 whereas the adsorption time was diminished by a factor of 1.5.

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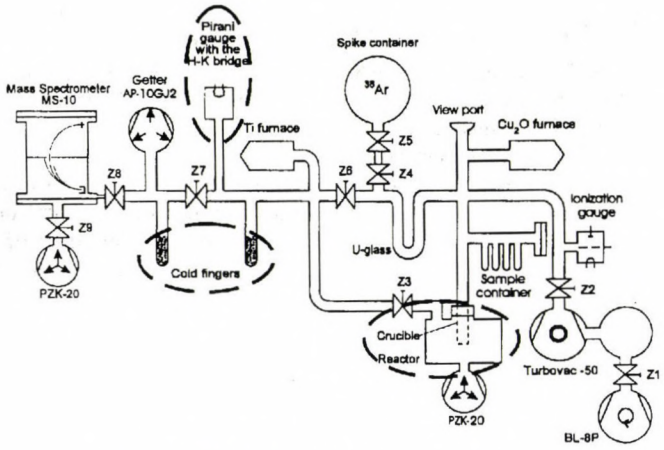

Fig. 1. The UHV line for Ar extraction and purification.

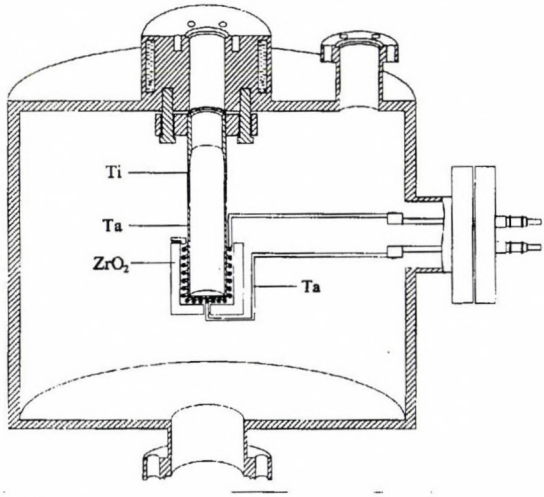

Fig. 2. The double-vacuum crucible for Ar extraction

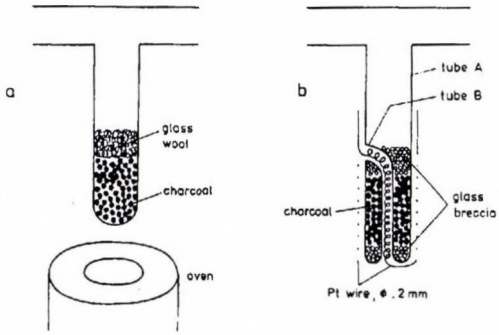

Fig. 3. Construction of the typical cold finger (a) and of that with improved construction (b)

CARBON AND OXYGEN ISOTOPES IN OFFSHORE AND CONTINENTAL MESOZOIC AND TERTIARY LIMESTONES, NE BRAZIL: THE K-T BOUNDARY AND TERTIARY CLIMATIC VARIATIONS

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Key words: Mesozoic limestones, Tertiary limestones, K-T boundary, paleotemperature, chemostratigraphy

INTRODUCTION

The Cretaceous-Tertiary (K-T) boundary is worldwide marked by faunal extinction, the cause of which has provoked countless and endless scientific discussions, and has mainly been ascribed to the impact of a bolide, or to intense volcanism. To better understanding the K-T transition, different isotopic studies (Sr, Pb, Os, Nd, O and C isotopes) have been carried out mainly in the northern Hemisphere. Although many contributors found in their studies support to a meteorite impact theory, this seems to be a matter far from solved.

In continental South America, the K-T boundary is recorded in limestones only in two localities: in the Pernambuco-Paraíba sedimentary coastal basin (e.g. Ashrof & Stinnesbeck, 1988; Albertão, 1994) in NE Brazil, and in Argentina. For the K-T boundary in the Pernambuco-Paraíba basin, some preliminary oxygen and carbon isotope data are available (Sial et al., 1992; Ferreira et al., 1994). There is no isotopic data for the K-T boundary in Argentina, however, where C. Nañez and N. Malumian (Geological Survey, Argentina) are studying at detail planctonic and benthic foraminifers (pers. communic., 1995).

Stratigraphic and sedimentological studies on the Tibau, Guamaré and Ubarana Formations (Potiguar basin), in the coastal area and offshore of the State of Rio Grande do Norte, NE Brazil, were recently carried out by Souza (1982) and Araripe & Feijó (1994), aiming as to oil exploration for PETROBRAS (Brazilian Oil Company). The Guamaré Formation is composed of a carbonate sequence, deposited on the continental shelf/slope from Neocampanian to Holocene (Souza, op cit.). There is no outcrop of this Formation on the continent. This way, this drilling by PETROBRAS offers a good oportunity to study the K-T boundary offshore, and climatic variations during the Tertiary.

GEOLOGY AND CHRONOSTRATIGRAPHY

Two limestone sequences in the Pernambuco-Paraíba coastal sedimentary basin are recognized, on the basis of fossil record and differences in age: the Maastrichtian Gramame Formation (deposited in warm, quiet marine water, below the waves bottom), and the Danian Maria Farinha Formation (deposited during a regressive phase of the sea; Tinoco, 1976). The K-T transition coincides with the beginning of a Tertiary regression. The contact between the two Formations is characterized by the vanish of Cretaceous fossils of the Gramame limestone, especially ammonoids and planktic foraminifera.

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Contribution n. 16 of the LABISE

The bottom of the Maria Farinha limestone is composed of a 60cm-thick breccious limestone, characterized by the presence of both Cretaceous planktic and Tertiary benthic foraminifera (Tinoco, op cit.). According to Albertão (1994) this layer is probably a tsunamite, formed by high energy process. The K-T limit is on the top of this layer, marked by a significative anomaly of Ir (up to 0.7 ppb) (Albertão, op cit.). A 10-cm thick clay layer, underlying the tsunamites, has been described in some localities. For this work we collected samples in a continuous profile starting at 13 m below and ending 11 m above the supposed K-T boundary in that site, including Gramame and Maria Farinha limestones and the breccia at the transition.

The Guamaré Formation is a carbonate sequence, which includes bioclastics calcarenites and calcilutites, laterally disposed between the Ubarana pelites and the Tibau sandstones. The fossil assemblage indicates Neocampanian and Holocenic ages for Guamaré Formation (Araripe & Feijó, 1984). Usually the marine fossil record points to very shallow depths during the Upper Tertiary for that sequence. The PETROBRAS provided us with the sampling carried out in six drill holes (1-RNS-8, 4-RNS-92, 1-RNS-133, 3-RNS-134, 3-RNS-115 and 1-RNS-124). Unfortunately samples represent an average of each 3m of corebit sampling. Even so, aiming as to the chemostratigraphy and identification of minor events recorded by oscillations of $\delta^{13}C$ and $\delta^{18}O$, isotope analysis in limestones or in the calcareous cement of sandstones were carried out. According to the stratigraphic descriptions from PETROBRAS, the K-T boundary was probably reached at 990m depth in the 1-RNS-134 drill hole, at 1125m (1-RNS-92), at 1380m in the 1-RNS-8 and at 2196m in the 1-RNS-133 drill hole. In these holes, sediments of the Ubarana, Guamaré and Tibau have been sampled.

SYSTEMATICS

Carbonate fractions of the offshore drill were hand picked under microscope to assure separation of quartz grains and other silicate clastic fraction. Whole-rock samples of both basins were washed with distilled water for separation of the clay fractions, and dried out under infrared light, before crushing to 200 meshes. Samples were analyzed by reacting with 100% H_3PO_4 according to Craig's method (1957). CO_2 released from this reaction was purified cryogenically and analyzed for oxygen and carbon isotopes in a VG Isotech Sira II mass spectrometer at the Stable Isotope Laboratory (LABISE), Federal University of Pernambuco, Recife, Brazil.

DISCUSSION AND CONCLUSIONS

The Pernambuco-Paraíba basin: $\delta^{18}O$ ranges for Gramame and Maria Farinha limestones are similar to each other, from -6.0 to -3.0‰$_{PDB}$ and -5.5 to -2.7‰$_{PDB}$, respectively. $\delta^{13}C$ values in the two Formations are positive, ranging from +1.0 to -3.5‰$_{PDB}$ (average +1.8‰; Gramame) and from +0.2 to +4.5‰$_{PDB}$ (average -2.0‰; Maria Farinha). Value at the matrix of the calcareous breccia is significantly different: $\delta^{18}O$ rises from - 4.0‰$_{PDB}$ just before that unit, to -0.9‰$_{PDB}$, while $\delta^{13}C$ drops from +1.9‰ to -5.5 ‰. A minimum in the δ13C is also observed elsewhere (e.g. Magaritz, 1989), and is interpreted by Ferreira et al. (1994) as a possible change in the biomass (strangelove effect, Hsu et al., 1985) or related to an increase in the oxidation of the organic carbon on land or on newly exposed continental shelf, due to a drop in the sea level.

Temperature estimates show similar range for Gramame and Maria Farinha limestones. The data indicate temperature of about 25°C just before the K-T boundary, followed by a marked cooling, down to 10°C, registered in the matrix of the calcareous breccia, and an increasing again after that, to around 25°C.

The Potiguar basin: at this stage of work, fifty eight samples were analyzed for sediments collected in offshore drilling, corresponding to Eocene to Miocene age interval. The sedimentation rate, estimated from biostratigraphic markers as biozones selected from data by PETROBRAS, varied from 2 to 2.5 cm/1000 years, regarding a constant rate.

$\delta^{13}C$ values in the analyzed drill holes are all negative, varying from -5.4 to -0.2‰$_{PDB}$. $\delta^{18}O$ varies from negative to positive, ranging from -5.2 to +1.6‰$_{PDB}$. The latter suggest temperature variations from a minimum of +10°C to a maximum of +40°C. These isotopic data reflect important climatic changes in the analyzed sediments during the Tertiary, as well as variation in the organic production, recorded by strong oscillations of the carbon isotopes.

The Early Eocene is characterized by negative $\delta^{13}C$ and $\delta^{18}O$ signature (PDB), with average temperature around 30°C (25° to 37°C). This rather high temperatures correspond to the high temperature-ocean water in South Atlantic, close to the Paleocene-Eocene transition, as observed by Shackleton (1986).

The Oligocene is characterized by large variation of both $\delta^{18}O$ and $\delta^{13}C$. $\delta^{18}O$ values decrease suddenly from positive (+1.5‰$_{PDB}$) to negative (around -2.5‰$_{PDB}$) and remain close to this value for about 40 m, until the depth of 800m is reached, which corresponds to ca.32 Ma. In this interval, variations of $\delta^{13}C$ are more pronounced with a tendency of values to increase, while corresponding $\delta^{18}O$ values remain almost constant. From 800 m depth up to 720m, there is a tendency of decreasing both $\delta^{18}O$ and $\delta^{13}C$ values, with marked oscillations. At this interval, more pronounced variations are observed for the $\delta^{13}C$, which drop down to -5.5‰$_{PDB}$, at about 750m depth. At the Oligocene-Miocene boundary (720m depth) there is a minimum in both $\delta^{18}O$ and $\delta^{13}C$ values, which drop to -5‰$_{PDB}$ and -4‰, respectively. Decreasing $\delta^{18}O$ values toward the Oligocene-Miocene boundary reflects temperature increase, a behavior opposite to the cooling of the South Atlantic oceanic water observed by Shackleton (1986). This temperature increase, accompanied by decreasing in $\delta^{13}C$ values (i.e. decreasing organic productivity), is probably a consequence of the basaltic volcanism (the 1.4 km thick Macau basaltic Formation, intercalated with rocks of the Tibau, Guamaré and Ubarana Formations is recorded in the drilling by PETROBRAS), and well documented in the nearby continental area.

The Middle Miocene is characterized by a sudden increase in the $\delta^{18}O$ values (from -3.0 up to +1.5‰$_{PDB}$), followed by a drop (down to -2‰$_{PDB}$). These incursions in $\delta^{18}O$ values are accompanied, in less extent, by increase of $\delta^{13}C$, reflecting a drop in temperature, to +10°C, at 13-15 Ma, probably corresponding to the major enlargement of the Antarctic ice-sheet.

These data demonstrate that although analyzed whole-rock samples are the average of each 3-meter corebit sampling, an idea of main paleoclimatic changes and organic production can be acquired. Carbon and oxygen isotope markers showed to be good chronostratigraphic tools.

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DEUTERIUM CONCENTRATION FROM WATERS OF DANUBE DELTA

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Keywords: deuterium, Danube Delta, isotope hydrology, natural tracer, isolines.

Introduction.

Water molecules with different isotopic composition have also different masses and those reality results in a variation of physical characteristics. Vapour pressure of these different molecules varies inversely proportional to mass. Vapour pressure rapport of two isotopical distinct molecule kinds is named separation factor and it depends on the temperature (Lewis et al., 1933). The same separation factor may also be defined as the concentration ratio of the isotope (in our case deuterium) from liquid and gaseous phase.

Ocean water is an immense reservoir as compared to water existing in gaseous phase. Deuterium concentration of ocean water might be considered as that of SMOW (155,76 ppmD/H, Craig 1961). Water vapour arising above the ocean in warmer areas has a higher deuterium concentration as compared to water vapour arising above the ocean at higher latitudes and consequently colder. Water vapour from oceanic areas with average temperature of 20°C has δD values of about -75 ‰ while in the areas with average temperature of 1°C it has δD values o about -95 ‰ (Craig et al., 1965). According to this matter of fact, south-west warm air masses originated in Mediterranean Sea bring water vapour with more deuterium content as compared to north-west cold air masses which bring water vapour with less deuterium content.

The precipitation produced by this air mass circulation have also different isotopic compositions.

The dependence upon temperature of the separation factor results in precipitation with higher δD values at lower latitude areas as compared to those at higher latitude areas. To the level of the whole planet the temperature variation may be followed as against to various factors. The most significant are latitude, altitude and the season. The variation of average temperatures between Equator and Poles results in different values of δD from precipitation. So, in equatorial areas, the precipitation has often δD values of about 2‰, while in the polar regions the δD values from precipitation decrease towards -488‰ (Friedman et al 1964). The temperature decreases also because of the altitude increase. At lower altitude there are δD values greater as compared to those of higher altitude. A diminution of δD values of about 4‰ to an altitude increase by 100m was established (Moser et al., 1970). The season succession is accompanied by a variation of the average temperature that produce a variation of δD values from precipitation and surface waters. The higher values of δD prevail in warmer season as compared to the values from colder season. A sequence of maximum and minimum δD was made evident for several years (Dansgaard, 1964).

Soil waters resulted from precipitation infiltration preserve the same succession of maximum and minimum values as a result of water infiltration through soil in a successive layer way (Feurdean, 1987). As soil infiltration waters represent the supplying source of phreatic bed it fallow also its water will show the same maximum and minimum value succession.

Therefore, surface waters directly influenced by precipitation show time and space variation of the δD values. Time dependent variation made evident by a maximum and minimum succession of δD values represents in fact a natural marking of waters that might be used in the hydrological studies. The utilisation of this effect of natural isotopic marking allows to carry out entire unpolluted hydrological studies.

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Methodology.

The main information source for a study by means of the effect of natural isotopic marking is the water samples drawn from the studied area. The sampling points as well as the samples themselves should fulfil certain conditions. For a sampling point these conditions are as follows:

-to be easily recognised both on map and on the terrain;

-to have a permanent characteristic.

The sample in its turn should fulfil the following conditions:

-not to be affected by another factors but the natural ones;

-to be sampled in a quantity enough to allow to repeat the isotopic analysis when ever it is necessary;

-sample draw should not produce disturbances or changes in the future evolution of the searched area.

Samples were drawn monthly between March and October. δD value measurement was made by means of a THN 202 B mass spectrometer with a measurement error smaller than ±0,1%.

Results.

The researched region is bounded on the North by Sulina branch, on the South by Sf. Gheorghe branch, on the West by Caraorman sand banks and on the East by Black Sea. Water samples were drawn from the following sampling spots: Caraorman channel, Sonda channel, Stinking back water, Sulina branch (at Sulina), Rosulet lake (north, central and south part), Rosu lake (north, south, east, west and central part), Puiu lake (north, south, east, west and central part) and Erenciuc lake (north, central and south part).

δD isolines with the values of September were plotted (fig. 1) and with the average values (fig. 2). These isolines allow to establish the increase direction for δD values that coincides with water flow direction.

Exceptions to the rule occur when water inflows with different δD values take place in a certain area (east area of Rosulet lake).

The main momentary flowing direction established on fig. 1 are:

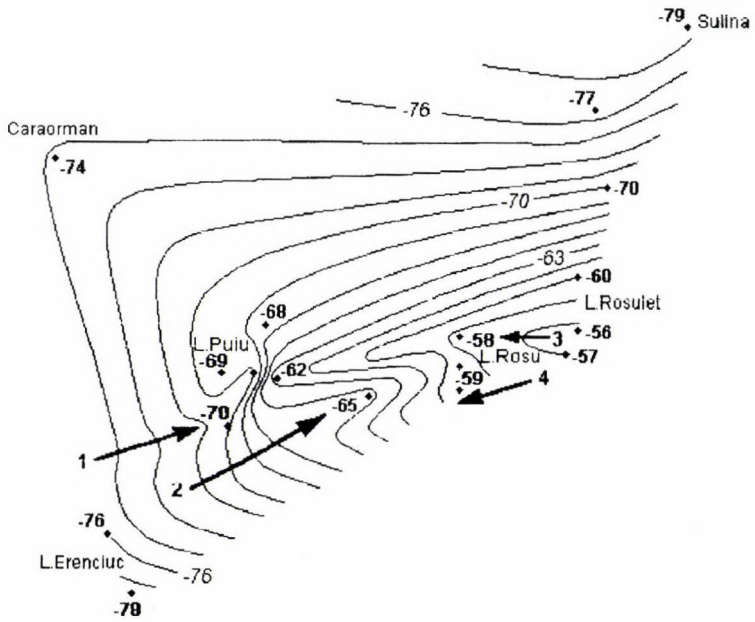

Fig. 1. Isolines for δD values (Sept. !993).

-from south-west (north part of Erenciuc lake) to south and central part of Puiu lake (direction 1);

-from south west (central part of Erenciuc lake) to west part of Rosu lake (direction 2);

-from east to the west part of Rosulet lake area and the south-east part of Rosu lake (direction 3 and 4).

We consider that sea water inflow (water of about -35 ‰) takes place according to these two last directions .

Water flows 1, 2 and 3, 4 respectively are oriented in the opposite directions towards western end of the Rosu lake and the area bounded by Puiu and Rosu lake. We consider the sand sediment from western part of Rosu lake as a result of this convergence of the likely flow direction.

The average flow directions corresponding to the period March-October 1993 might be established from fig. 2. These directions are:

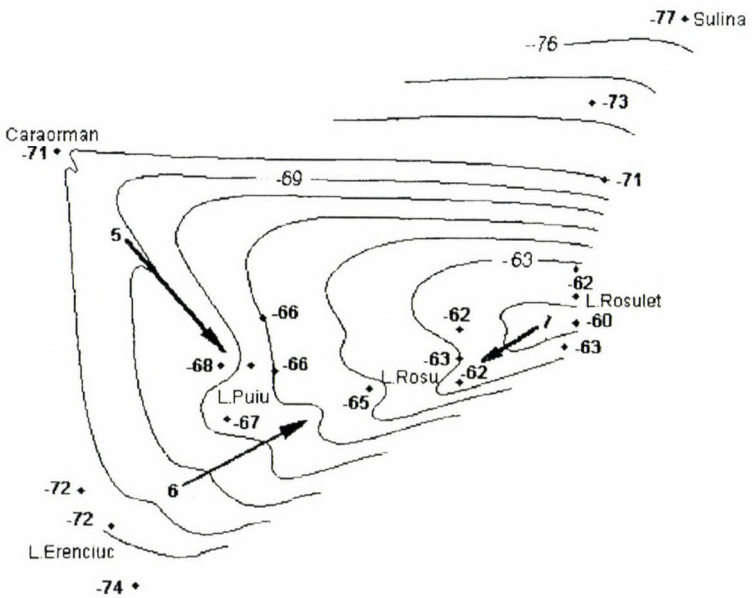

Fig. 2. Isolines for δD values (average values).

-from north-west towards Puiu lake following Caraorman channel (direction 5);

-from south-west (central part of Erenciuc lake) west ward of Rosu lake (direction 6);

-west ward in the south part of Rosulet lake and east area of Rosu lake (direction 7).

The sea water inflow takes place according to this direction (water of about -35 ‰). The average flow directions converge on the same area (west part of Rosu lake and the area bounded by Puiu and Rosulet lakes) as the momentary flow directions do.

Conclusions.

The isoline for momentary δD values and average values respectively lead to the following conclusions for the researched area:

-a water flow direction is from Erenciuc lake towards west, end of Rosu lake. This direction result both from the momentary values (month of September) and the average values;

-average values only show a flow direction from north of Puiu lake towards to north-central area of Rosu lake;

-the east part of the researched area we think to be under the influence of sea water both by a direct way of communication with the sea (Sonda channel) and an indirect one by sea water contribution of the under current through the part lying to east end of Rosu lake.

In view of δD values for the sea water and for the Danube Delta waters we consider the contribution of the sea water being comparatively small (do not exceed 10%).

We might consider the substantial sand sediment at the east end of Rosu lake result from the convergence of water flow directions in that area as suggested by the water flow direction in Rosu and Puiu lake's area.

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ORIGIN OF BANK FILTERED GROUNDWATER RESOURCES COVERING THE DRINKING WATER DEMAND OF BUDAPEST, HUNGARY

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Keywords: bank filtered water, stable oxygen isotope, pollution, hydrology

INTRODUCTION

The drinking water demand of more than two million inhabitants of Budapest is mainly covered by bank filtered water of the River Danube. The ratio of the Danube water and the background shallow groundwater in the supplied water is very important question related to drinking water quality. The background shallow groundwater is potentially polluted by agricultural activity and communal waste water of unsewered settlements. The mixing of these two types of waters has been investigated by stable oxygen isotope ratio.

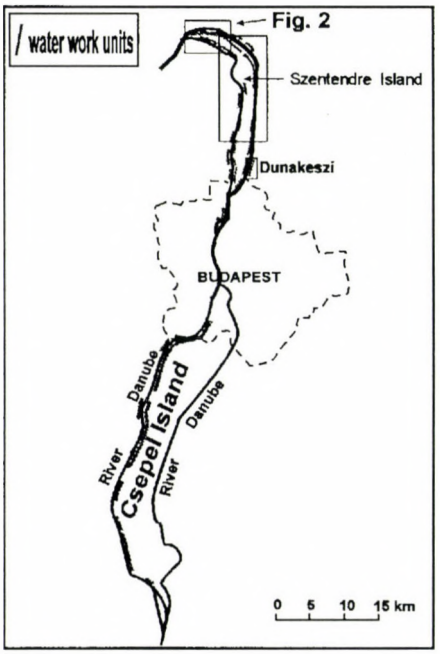

Fig. 1 Sketch map showing the investigated area

The bank filtered wells are located on both side of the Danube north and south of Budapest, in Budapest, and on the bank shores of the Szentendre Island and Csepel Island (Fig. 1).

In the first stage of our project we have studied different parts of the Szentendre Island and the area of the Dunakeszi Water Works on the left bank of the River Danube. Here we discuss in details only the most northern part of the Szentendre Island. The $\delta^{18}O$ values are measured, evaluated and compared to some chemical components of the water.

METHODS USED

The basis for determining the origin of the drinking water supplied from bank filtered wells is the fact that the $\delta^{18}O$ value of Danube water (-11 — -12‰) is significantly different from the locally infiltrated groundwater (-9.3‰). Using this difference we can calculate the mixing ratio of Danube water/background shallow groundwater by $\delta^{18}O$ data measured in working drinking water wells according to the following equation:

$$X_{Danube} = \frac{\delta^{18}O_{well} - \delta^{18}O_{groundwater}}{\delta^{18}O_{Danube} - \delta^{18}O_{groundwater}} * 100\ (\%).$$

RESULTS

Stable oxygen isotope data of the wells sampled are plotted on Fig. 2a-b. At the same time the main and trace element content of water samples has been determined (e.g. nitrate is plotted on Fig. 2c).

DISCUSSION

The $\delta^{18}O$ value of the Danube water in the vicinity of Dunakeszi (Fig. 1) is -11.52‰ (one sampling). The multi-annual mean $\delta^{18}O$ value of the Danube water at Vienna is -11.7‰ (Rank, person. com.). According to sporadic data (Deák et al., 1991), $\delta^{18}O$ value of the River Danube in the vicinity of the Szentendre Island is a little more positive, so in first approach the measured value of -11.5‰ is appropriate for calculating the mixing ratio of Danube water/background water. The multi-annual mean of infiltrating precipitation in Hungary is -9.3‰ (Fórizs 1995).

Northern part of the Szentendre Island

All the wells are located on island. The $\delta^{18}O$ value of the majority of the operating wells (T/I.100, T/II.5, T/II.2.cs., K16) are identical with that of the Danube (Fig. 2a-b). In these cases we can state that the supplied water is 100% of Danube origin. The $\delta^{18}O$ values of three wells (T/II.31, K 7.cs., K64) are less negative than that of the Danube indicating that these supplied waters have background water component in the range of 20-40%.

The $\delta^{18}O$ values of the observation wells ranges between -9.6 and -10.9‰. These values are more negative than that of the local infiltration, so the shallowest groundwater of the island is a mixture of Danube water and the local infiltration. Going from the Danube to the center of the island, the Danube water component is less and less (Fig. 2b, A and B profiles). The Danube "flows" under the island.

There is a positive correlation between the $\delta^{18}O$ values and the nitrate, chloride and sulfate content (Fig. 3). The less negative the $\delta^{18}O$ value the higher amount is the pollutant concentration, i.e. as the infiltrated precipitation component of the water is higher, the pollutant concentration is higher. This trend is a clear indication that the source of the pollutants is on the island and not the Danube Water.

Acknowledgement This research project has been financed by the National Scientific and Research Fund (OTKA T0114968) and the International Atomic Energy Agency (Contract No. 8126)

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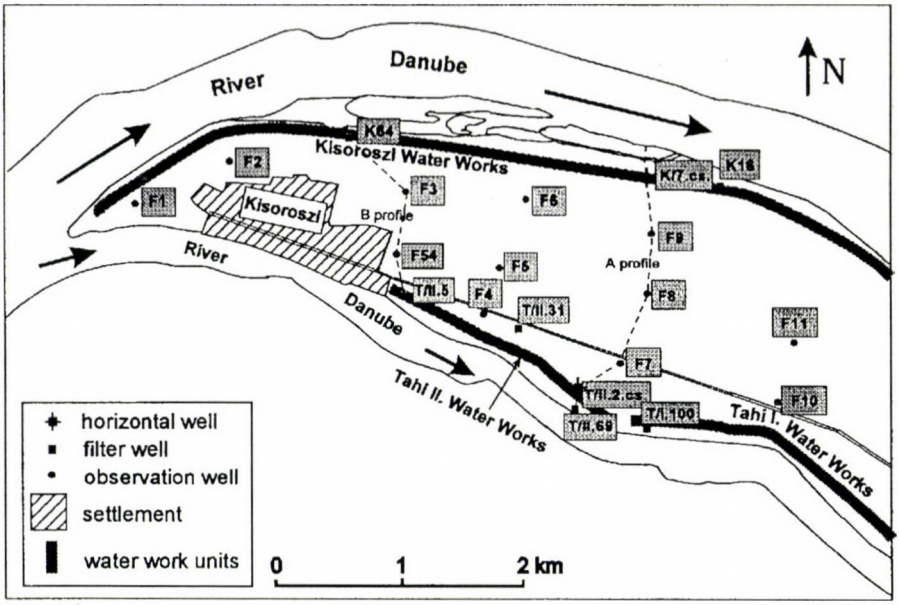

Fig. 2a. Sketch map of the northern part of the Szentendre Island showing the names and locations of the sampled wells.

$\delta^{18}O$

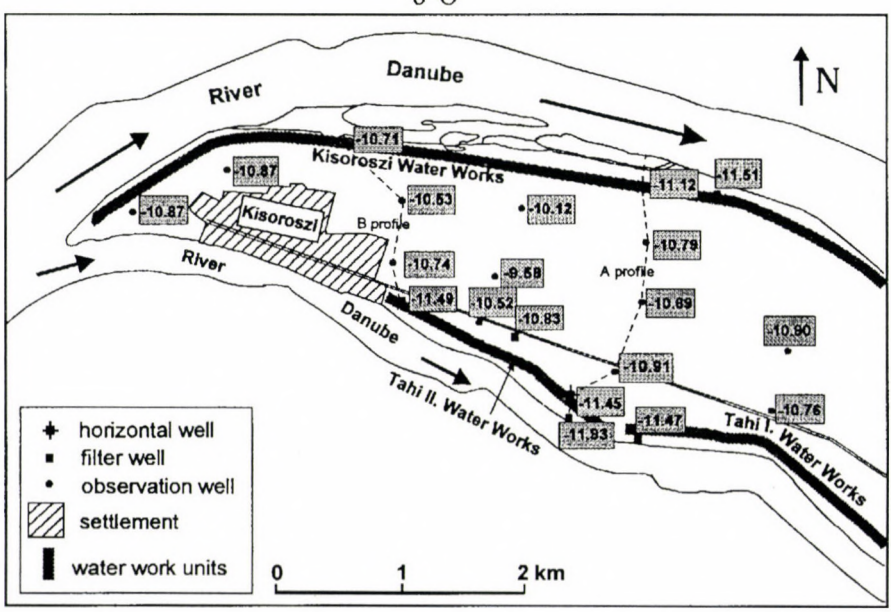

Fig. 2b. The stable oxygen isotope compositions of the wells sampled on the northern part of the Szentendre Island.

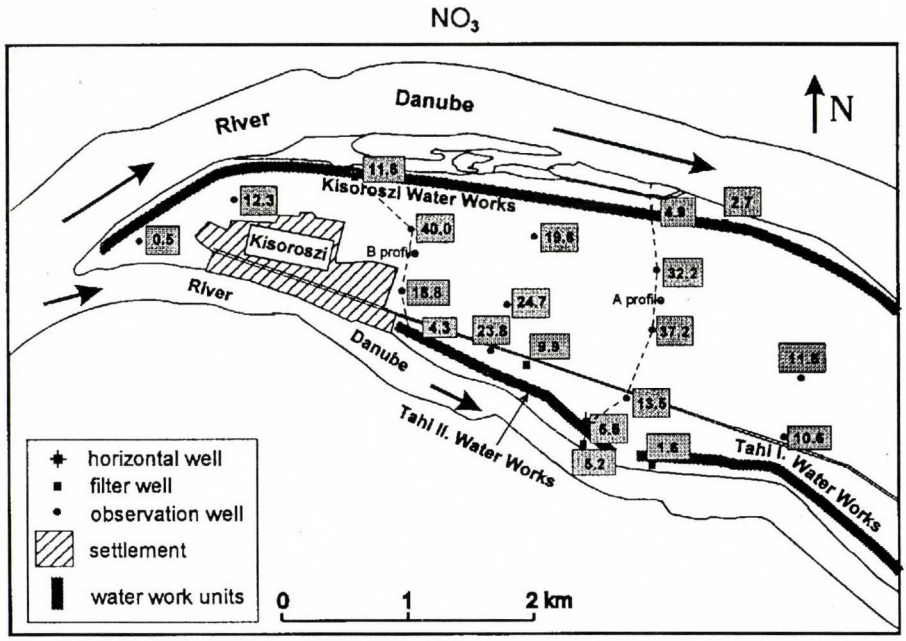

Fig. 2c. The nitrate content of the wells sampled in the northern part of the Szentendre Island.

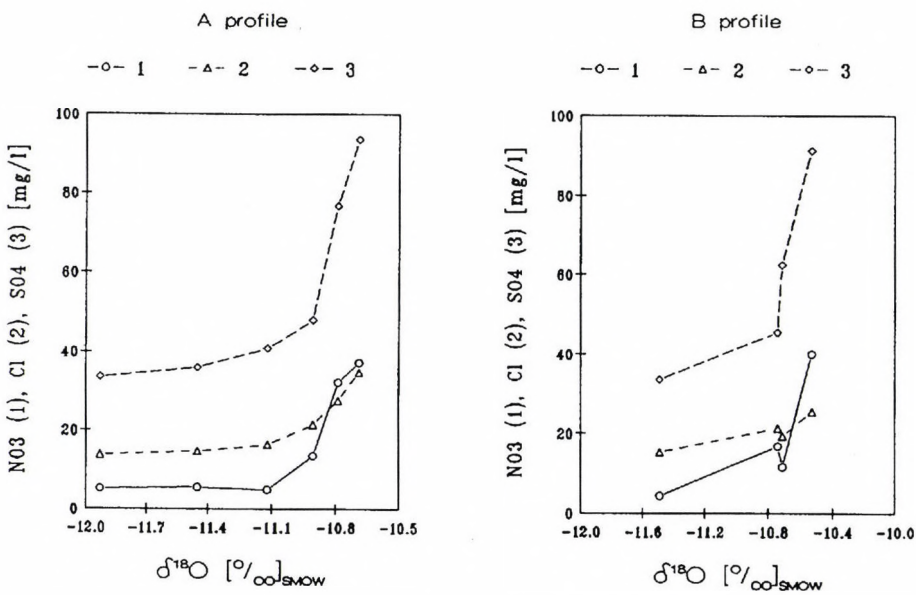

Fig. 3. Nitrate, chloride and sulfate content vs. stable oxygen isotope composition in A and B profiles (see Fig. 2a).

Origin and Rb-Sr isotope age of pegmatites from the Western Tatra Mts. - a revised geochemical study.

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Keywords: pegmatite, partial melting, isochrone age, initial ratio.

In the Polish part of the Western Tatra Mts. pegmatites could be found mainly within the metamorphic cover of the granitoid pluton, rarely in the granitoid body itself. They occur as lenses and veins ranging in size from a few centimetres to a few metres. Mineralogy of pegmatites in question is rather simple: alkali feldspars, quartz and micas are the main components, apatite, zircon, allanite and turmaline could be found as subordinate minerals. Secondary minerals are represented by: chlorite, sericite, kaolinite, celadonite and illite/smectite (Gawęda, 1993).

Pegmatites from the Polish Western Tatra Mts. are peraluminous in composition. Almost all plots of their normative compositions assemble in the central part of the Ab-Or-Q triangle, near the „thermic valley" (Luth & Tuttle, 1969; Fig.1). Many samples of gneisses and migmatites were analysed from the studied area (Gawęda & Burda, 1995; Gawęda & Piwkowski, 1995). Some of them, being wall-rocks of the investigated pegmatites, have the compositions plotting near the „thermic valley" and are peraluminous in composition. The trace element content is rather low and similar in pegmatites and in their host-rocks. It should be noted that in some regions of the Western Tatras crystalline complex, where pegmatites are lacking, the compositions of source rocks (gneisses, migmatites, mica schists) are not favourable for producing low temperature minimum melts (their plots lie far from cotectic plane in the Ab-An-Or-Q tetrahedron; Gawęda & Burda, 1995).

Representative whole-rock samples from 5 locations within the Upper Kościeliska Valley were chosen for isotopic investigations. The range of Rb/Sr and $^{87}Sr/^{86}Sr$ is wide (Fig.2), but the scatter of the points along the regression line is small (r = 0,9993, ***MSWD*** = 3,25). The calculated isochron age for the pegmatite suite from the considered area is 345 ± 9,5 Ma. The initial ratio (***IR*** $^{87}Sr/^{86}Sr$) is 0,70625 ± 2.

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DISCUSSION

The obtained initial $^{87}Sr/^{86}Sr$ ratio for pegmatites from the Polish part of the Western Tatra Mts. is typical for mantle-derived magmatic rocks. According the previous investigations of Burchart (1968) the Tatra Mts. granitoids have the isotopic characteristics typical for crustal partial melts (***IR*** = 0,715).

Taking into account both the geological position and geochemical characteristics of the pegmatites in question two possibilities should be considered:

1. The pegmatites are connected with mantle-type granitoid magmatism;

2. The pegmatites are partial melts with the isotopic features inherited from the source rocks.

The Tatra Mts. granitoid intrusion is 330 Ma years old and it is probably S-type or mixed I-S type (Burchart, 1968; Janak & Kohut, 1994). In the Upper Kościeliska Valley evidences of partial melting in small scale resulting of *in situ* crystallization of graphic granites (Gawęda, 1994) were noted. In metamorphic complex of the investigated area the PT-conditions of upper amphibolite facies were favourable for small scale partial melting, especially in zones of decreasing pressure (tectonic fissures and faults). The geochemical (and isotopic) features of the pegmatites in question seem to be inherited from the source rocks. In the metasedimentary complex of the Polish Western Tatra Mts. intercalations of amphibolites are present. These amphibolites are thought to be (at least partly) the products of submarine, rifting-related volcanism of unknown age (Caledonian ?) (Narębski & Wichrowski, 1973 ; Gawęda & Kozłowski, 1995). As a result of melting of the metapelitic-metapsamitic rocks alternating with mantle-derived basaltic material the hybridic magma might have been produced. In the metamorphic complex under consideration the conditions of P-decrease and T-increase were noted (P = 2-4 kbar ; T = 750-780°C; Gawęda & Burda, 1995). This stage of evolution, probably connected with the heat supplied by the granitoid pluton, was the most favourable for pegmatite melt generation. The relatively old age (345 ± 9,5 Ma) of pegmatites in question is probably a record of the early Variscan metamorpho-magmatic events in the Western Tatra metamorphic complex. The previously accepted age of pegmatites in question (280 ±80 Ma - Burchart, 1968) seems to be - in fact - rather the age of hydrothermal activity. In the sampling area (Ornak vicinity - see sample descripition in: Burchart, 1968) hydrothermal alterations of all rocks are extremaly strong.

The interrelation between the age of metamorphic processes and pegmatite emplacement as well as the Rohače granitoid origin is now investigated by the author.

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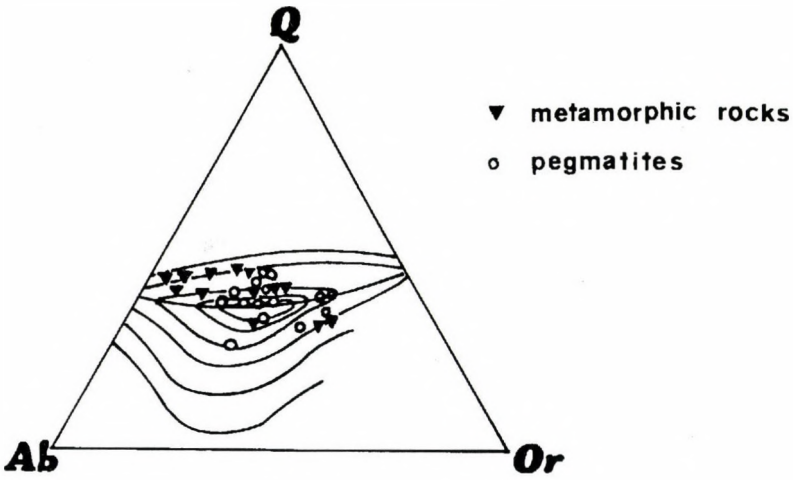
Q
Ab
Or
metamorphic rocks
pegmatites

Fig. 1

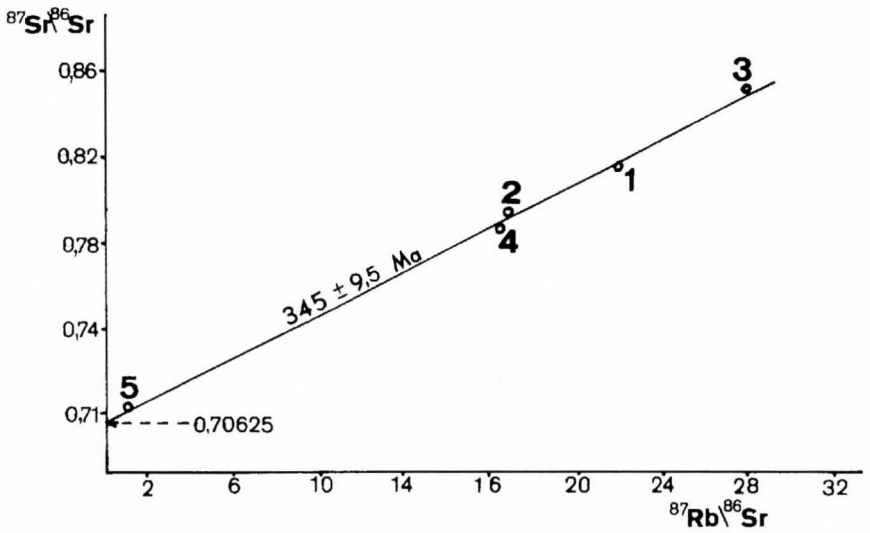
87Sr\86Sr
0,86
0,82
0,78
0,74
0,71
0,70625
345 ± 9,5 Ma
1
2
3
4
5
2
6
10
14
16
20
24
28
32
87Rb\86Sr

Fig. 2

Seasonal variation in the Oxygen and Hydrogen isotope composition of an inland prairie river, Bow River, southern Alberta, Canada

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Introduction

The "continental effect" is expressed as a progressive inland depletion in the heavy isotopes of precipitation, and resultant surface water, due to Rayleigh type distillation. The continental effect is even more pronounced over mountainous areas where orographic uplift enhances precipitation. In a recognizance study, Yonge et al. (1989) sampled surface water across southwestern Canada, from the Pacific Coast, across the Great Divide and into the continental interior. They note that from the Pacific Coast to the Great Divide (the divide between Pacific and Atlantic/Arctic drainages) that the δD of water bodies follow a typical Rayleigh distillation pattern. However, this trend abruptly changes at the continental divide to a trend of increasing δD inland. Standard models of evapotranspiration can not explain such a trend. Young et al. (1989) suggest that this abnormal trend in δD is likely related to the weather systems from which the surface water originates.

This study examines the Bow River Basin, a river basin east of the Great Divide, in order to investigate the "reversed" continental effect observed by Yonge et al. (1989). In addition seasonal variations in the isotope composition of the Bow River where examined to determine relative inputs of meteoric and ground water to the river system. Four sample sets, representing the major seasons from fall of 1993 to summer of 1994 (10/93 - fall, 01/94 - winter, 05/94 - spring, 08/94 - summer), were collected along the Bow River and its major tributaries, representing a range from base flow to high flow conditions.

There are two main weather systems that bring the majority of precipitation to the Bow River Basin. The dominant source of precipitation is westerly winds that bring precipitation to the basin in the fall and winter. In spring and summer precipitation is largely derived from southerly winds that swing north around a high pressure system that commonly develops over the state of Idaho. In the winter months the Rocky Mountains have a strong rain shadow effect on the westerly flow, creating progressively drier conditions from west to east. In the spring and summer this affect is reversed, where air systems from Idaho rise orographically against the eastern slopes of the Rocky Mountains, creating progressively drier conditions from east to west.

The isotope composition of precipitation in the Bow River basin varies widely, with $\delta^{18}O$ ranging from -2.2 to -44.0‰ and δD from -5.5 to -333‰. The heaviest precipitation is associated with spring and summer rains derived from the Idaho High, whereas the lightest is associated with weather systems derived from Arctic fronts. Westerly winds carry precipitation with intermediate isotope compositions ($\delta^{18}O$ = -20‰, δD = -155‰). Precipitation has a weighted average meteoric water line (MWL) of: $\delta D = 8.1\ \delta^{18}O + 8.0$, similar to the global MWL.

Variation in δD of tributaries to the Bow River

Figure 2 shows the variation in δD of tributaries along the length of the Bow River. For each season there is a trend of increasing δD with distance. This trend is similar to that observed by Young et al. (1989) and is contrary to standard Rayleigh fractionation models that predict a progressive inland depletion in the heavy isotopes. Normally when waters become enriched in D it is interpreted to be due to evaporation. In this case, two features suggest that evaporation is not the primary control on the observed enrichment. First, samples from the spring show the greatest rate of increase, however this is when evapotranspiration would be relatively low. Secondly the Elbow (ER) and Highwood (HR) rivers do not follow the inland enrichment trend, they plot to the right of the slope. If the δD of the tributaries are plotted against the distance of their headwaters from the Great Divide (Fig. 3), then the Elbow and Highwood rivers fit the observed trend of inland enrichment in heavy isotopes (with δD increasing at a rate of 30‰/100 km in the spring and 6‰/100 km in the fall). This suggests that the δD of the tributaries is a function of their source area rather than evaporation.

The Bow River Basin receives the majority of precipitation from two sources, westerlies and upslope winds from the Idaho high. The stable isotope composition of precipitation derived from the Idaho High is more enriched in heavy isotopes than precipitation derived from the westerly winds. Due to the reversing rain shadow effect over the Rocky Mountains, precipitation from these two weather systems effectively mix, with moisture from the Idaho high forming a larger proportion of the total precipitation eastward. Thus the observed trend of δD increasing inland is related to the mixing of weather fronts rather than evaporation effects. The mixing effect is greatest in the spring (30‰/100 km) when weather from the Idaho High is a significant source of precipitation in the eastern ranges of the Rocky Mountains, whereas the western Ranges are adding significant fluxes of snow melt (derived from westerly flows).

Seasonal variation of $\delta^{18}O$ and δD in the Bow River

The $\delta^{18}O$ and δD isotope composition of the Bow River have a best fit line of: $\delta D = 4.0\ \delta^{18}O - 75$ ($r^2 = 0.94$). The low slope, as compared to the local MWL, suggests that groundwater is a dominant source of the Bow River (averaged by time, not by volume). However, when samples from each season are plotted separately, seasonal variations in the amount of meteoric versus ground water input are evident.

Figure 4 illustrates the best fit lines for each season samples were collected. The slope of the best fit lines steadily increase from fall to summer. This trend of increasing slope represents the relative amounts of ground water versus meteoric water input into the river. The fall and winter samples represent low stage flow, with maximum groundwater input into the river. Although spring is the high flow stage of the river, related to melting of the snow pack, the samples in summer have a higher slope, representing maximum meteoric water input. Presumably, if the snow melt was translated directly to runoff, the river would have an isotope composition close to the MWL. There are two extremes in the way melting snow enters stream networks (Krouse et al., 1978): 1) overland flow, and 2) seepage through the ground. In the first case the streams would show a meteoric water signature coincident with the rise in stage, whereas in the second case the melt water will penetrate the ground and displace groundwater water into streams. In this event, the rise in stage will not be accompanied by a significant shift in the isotope composition of the stream water. Isotope data for the Bow River indicate that the high spring discharge, related to melting of the snow pack, has a significant groundwater component.

Conclusions

The anomalous trend of increasing δD inland, first reported by Yonge et al. (1989), is related to the reversed rain shadow effect of the Rocky Mountains, and the resulting east-west mixing of precipitation from the two predominant weather systems (westerly flow, and wind derived from the Idaho High). This indicates that caution should be used, particularly in mountainous areas, in applying Rayleigh type fractionation models to interpreting trends in the stable isotope composition of surface waters. Even in none mountainous areas it is important to quantify how weather systems bring moisture to a basin being studied before fractionation models can be applied to surface waters.

Stable isotope data indicate that ground water is an important source of the Bow River through the year. If we use 50 m^3/s as the average groundwater discharge into the Bow River, then groundwater accounts for 40% of the 4 km^3 average annual discharge of the Bow River. This has important implications for water use. The Bow River is the primary source of water for most people in the basin; currently 61% of the average annual flow is licensed for use. As the

population in the basin grows, ground water is seen as the next alternative source. If ground water resources are exploited in the basin, there is a danger that it will reduce the natural flow of the river.

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Figures

Figure 1. Plot of δD of tributaries versus the distance of their confluence along Bow River. PR = Pipestone River, SR = Spray River, KR = Kananaskis River, GR = Ghost River, JC = Jumpingpound Creek, ER = Elbow River, NC = Nose Creek, HR = Highwood River.

Figure 2. Plot of δD of tributaries versus distance of the headwaters of the tributaries from the Great Divide. Letter codes are the same as in Figure 1.

Figure 3. Best fit lines for each sample set, with the local MWL and average isotope composition of precipitation derived from westerlies and the Idaho High.

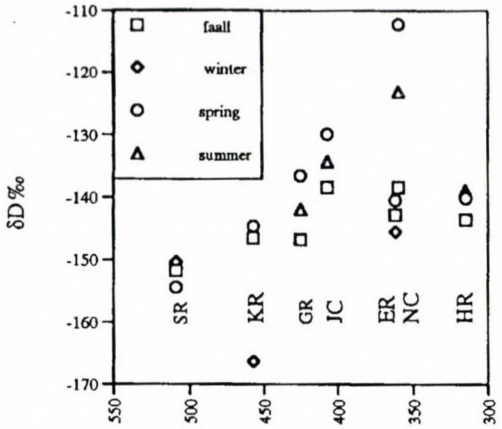

Figure 1 distance (km) along Bow River of the tributaries confluence

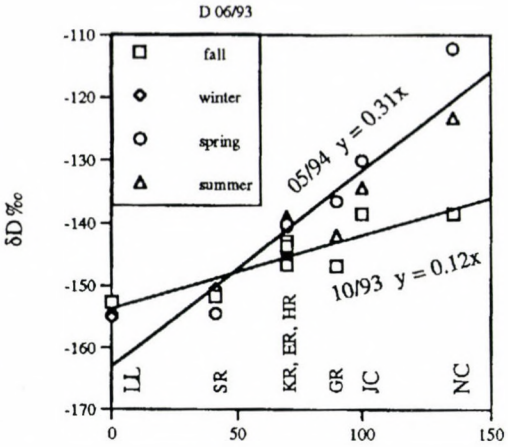

Figure 2 distance (km) of headwaters from the Great Divide

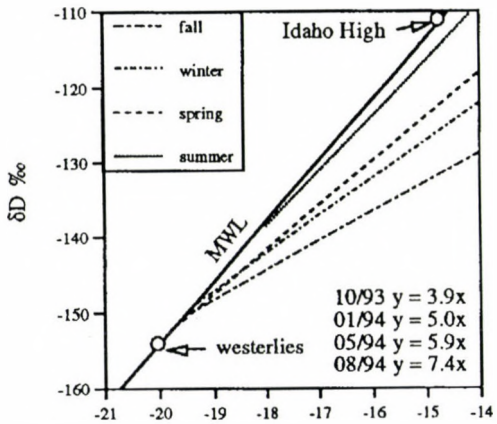

Figure 3 δO ‰

K/Ar dates of some Miocene potash salts from Carpathian Foredeep

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Keywords: argon 40, dating, mass-spectrometry, Miocene, potassium 40, salts

Introduction

The stratigraphy of Miocene salt deposits in Carpatian Foredeep is still controversial due to lacking biostratigraphical markers (Koriń 1994). This problem may be solved, however, by the methods based on radioactivity of potassium being developed in Lublin laboratory (Durakiewicz and Hałas 1996, Durakiewicz 1996). Two possibilities may be used: (1) investigation of tuffic material incorporated into salt rock, the best mineral in this case is sanidine, (2) investigation of potash salts, the best material in this case is langbeinite due to the highest argon retentivity.

By far we selected the second approach since potash salt deposits are very common in Dnister-river valley (Fig. 1). The potassium-bearing minerals which are abundant in that area are listed in Table I. We have dated a few samples from Stebnyk and Kalush deposits.

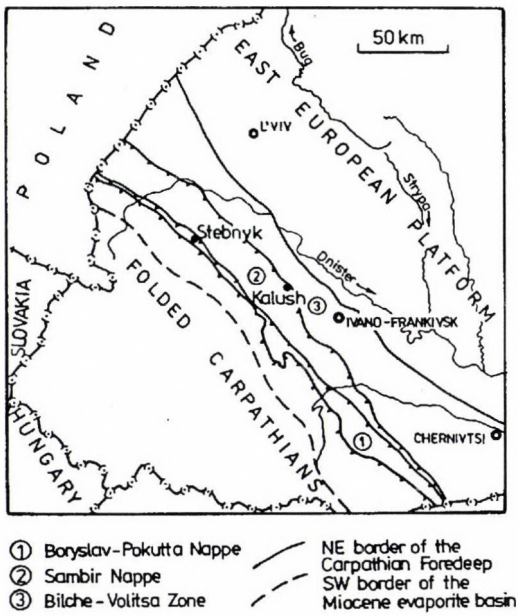

Fig. 1. Simplified map of study area.

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Table I. Selected properties of potash salts which occur in Miocene formations in Carpatian Foredeep.

Mineral	Chem. formula	Theor. % K	Decomp. T [°C]	Ar retentivity (ar)
Langbeinite	$K_2Mg_2(SO_4)_3$	18.84	~1100	excellent[1, 2, 3]
Polyhalite	$K_2MgCa_2(SO_4)_4*2H_2O$	12.97	~1100	very good[4]
Kainite	$4[KMg(ClSO_4)]*11H_2O$	15.99	~1000	good (?)
Sylvite	KCl	52.47	770	good[1]
Syngenite	$K_2Ca(SO_4)_2*H_2O$	23.81	~1000	ar=?
Carnallite	$KMgCl_3*6H_2O$	14.07	(?)	hygroscopic, ar=?

[1]Aldrich and Nier (1948) [3]Lippolt and Weigel (1988)
[2]Lippolt and Oesterle (1977) [4]Pilot *et al.* (1994)

Analytical procedures

Pieces of salt rock were crushed and sieved. The grain fraction from 0.3 to 0.5 mm was splitted for %K determination by atomic absorbtion spectrometry and radiogenic argon measurement by static vacuum mass-spectrometry. Aliquots of ca. 50 mg were melted in double-vacuum crucible of the Ar extraction-purification line. Pure ^{38}Ar was used as spike for mass-spectrometrical determination of ^{40}Ar. The atmospheric argon contamination was determined from peak ^{36}Ar. An example of experimental conditions is shown in Table II.

Table II. Analytical data on langbenite (sample no. 3).

Weight [mg]	% K	^{38}Ar spike [pmol]	$^{40}Ar/^{38}Ar$	$^{40}Ar/^{36}Ar$	% $^{40}Ar_{rad}$	Date [Ma]
48.0			3.180	641.2	53.9	**13.57**
47.8	16.65	11.007	3.131	643.8	54.1	**13.47**
50.0			3.182	658.2	55.1	**13.33**

Results and discussion

Each sample was analyzed independently three times and standard error of date was estimated statistically, which seems to be more reliable than use of the error propagation formula. Moreover, the dispersion of dates for individual sample may also reflect the influence of argon extracted from contaminants like clay minerals, meteoritic dust, clastic material etc, which are present in salt rock. The gray polihalites may be particulary affected by Ar extracted from the contaminants. For this reason the oldest dates sem to be not reliable. Another analytical approach must be applied for highly contaminated salts. In future studies we plan to dissolve "powderd" to 0.01 mm salts in water. With this method we will be able to extract Ar from salt only. Moreover, the potassium and ^{40}Ar content will be determined in the same sample, which

is impossible by the thermal extraction method, ie. by heating the samples up to melting point or decomposition temperature.

Table III. Average dates of investigated samples.

Sample description	Location	% K	Date ± stand. dev.
Langbeinite (No. 3), transparent	Kalush	16.65	13.5±0.1 Ma
Polyhalite (No. 6), red and transp.	Kalush	11.13	10.5±0.1 Ma
Polyhalite (No. 5), gray	Kalush	8.84	23.6±0.8 Ma
Langbeinite (No. 118), transparent	Stebnyk	20.10	14.1±0.5 Ma
Polyhalite (No. 4), gray	Kalush	9.82	16.6±0.3 Ma
Syngenite, transparent	Kalush	23.16	0.0 Ma
Kainite (No. 7), transparent	Kalush	10.04	7.8±0.2 Ma

Referring to Table III, one may state that all the dates obtained fall into the Miocene interval which extended from 23.7 to 4.8 Ma (Berger 1992). The only exception is transparent syngenite which either might be formed recently or it has extremely low argon retentivity. The most reliable dates are based on pure transparent langbeinites. These dates fall into Badenian which extends from 16.5 to 13.5 Ma (Berger 1992).

Transparent polyhalite and kainite have 10.5 and 7.8 Ma, respectively. It is not clear whether kainite has sufficient argon retentivity and whether this mineral was formed at time of salt crystallization from the sea-water. Much of polyhalite in the geological section has long been recognized as a replacement of gypsum or anhydrite, although there are some doubts as to whether this process may have taken place at a later time, after consolidation. According to study of recently formed polyhalite in the Gulf of Mexico, polyhalite diagenetically replacing gypsum are formed very early (Holser 1966). Our study is in gradual progress. It is belived that stratigraphical positions can be elucidated from careful analysis of selected potassium minerals.

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S, O, C ISOTOPIC SIGNATURES OF THE LATE MIOCENE PANNONIAN LAKE

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Keywords: sulphur, carbon and oxigene isotope, diagenesis, lake sedimentation, Pannonian Basin

The aim of the present project, sponsored by the Hungarian National Science Foundation (OTKA NO. F7373), was to introduce sulphur, carbon and oxygen isotope measurements for late Miocene Pannonian brackish lake deposits.

The del. 34S ratios of 40 pyrite and marcasite samples are at an extremely wide range, from -42.8 to +19.6 permil. Disregarding the few samples of hydrothermal origin the frequency distribution of data is unimodal. The +0.1 permil mean value is much more positive than average marine data (-20...-30 permil). The explanation is that the low sulphate concentration of the brackish water was a limiting factor in bacterial sulphate reduction and in the fractionation of sulphur isotopes. In addition, the prevailing deltaic sedimentation was characterised by extremely high depositional rates (500-2000 m/Ma). Sedimentary pores closed rapidly which hindered the continuous sulphate supply from the overlying water. As a consequence heavy pyrites were formed through the repeated redistribution of 34S. The "isotopic pool" model can not be excluded as an alternative answer for depleted isotopic composition. Between 13-9 Ma the Pannonian inland sea was totally isolated and deep, periodically anoxic "starving" subbasins developed with organic- and pyrite-rich pelitic sedimentation. Unfortunately, primary sulphate minerals are totally absent from this sequence to check the theory.

Dolomarls, dolomitic mudstones and dolomites were penetrated by several continuously cored deep boreholes in the late Miocene sequence. The 0.1-2.0 m thick massive, greenish grey, grey or dark grey lenticular, laminated Pannonian ferroan dolomites were deposited in delta plain and lake environment. Both the coexisting calcite and dolomite phases were measured for their carbon and oxygen isotopic composition in 82 samples. A wide spectrum of del. 13C and del. 18O values of the dolomites were observed: -28.9 to +15.6 and -10.6 to +4.1 permil, respectively. On the C/O crossplot diagram the two groups of data clearly show the early diagenetic zones of sulphate reduction and methanogenesis. A limited number of samples show the isotopic impact of burial decarboxylation. In the two latter group the del. 13C values of dolomite phases are 2-3 permil higher than the coexisting calcites, in accordance with the direction of diagenetic processes. In contrast, the del. 13C values of dolomites formed during bacterial sulphate reduction are 3-6 permil lower than that of the calcites. Besides diagenesis the depleted del. 18O values in general provide an evidence of the diluting effect of terrestrial waters entering the Pannonian lake.

The effects of early diagenesis on organic stable carbon isotope ratio changes and maceral composition of Miocene lignites in N-Hungary

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Keywords: lignite, coal petrology, carbon isotope, Lower Miocene, Hungary

The term coal facies is mainly determinated by the peat-forming vegetation, water and nutrient supply, marine influence and fire. The preservance of organic matter depends on early diagenesis, where chemical changes like transformation from cellulose and lignin to fulvo and humic acids are the main processes.

Former studies on recent and ancient wood samples (Hatcher, and Breger, 1981) showed that there is a linear correlation between chemical composition and δ^{13} C ratio changes during early diagenesis (Spiker and Hatcher, 1987). Degradation and loss of cellulose in buried wood may result $^{13}C/^{12}C$ ratio changes (Spiker and Hatcher, 1984).

Coal petrological studies were carried out in the frame of paleoenvironmental reconstruction of early Miocene lignite seams (Hámor-Vidó, 1992, 1993). In those works we tried to show an evaluation of the mire belt system using maceral analysis. Coal petrological studies helped us to determine the state of the organic matter (preservance, grade of degradation, transportation). The type of coal facies was interpreted by the help of maceral analysis. Four facies were distuingished in double triangle diagram. The three peaks of the upper triangle represent swamp, marsh, aquatic facies respectively. The swamp facies dominantly consists of woody origin macerals and sclerotinite. In the marsh facies gelinite, detrited woody materials, pollen cuticular and humic leaf remains are the major constituents. In the aquatic facies carbominerite minerals, alginites and sporinite amorphous organic material are the most dominant macerals. In the lower triangle inertinites and humodetrinites are the dominant macerals and the fourth peak represents terrestrial, or allochtonous peat forming environments.

Comparing results of different methods we chosed 53 samples from two coal seams in the East Borsod region. The studied samples were mainly coals, but in some cases we made measurements on coaly shales and shaly coals as well. In each of our samples we determined the coal facies and organic stable carbon isotope ratio. Beside coal facies analysis gelification index was given to show the preservance of organic matter. Gelification Index determines the ratio of well preserved and degraded humic macerals similarly as used by Von der Brelie and Wolf (1981).

$$\text{Gelification Index} \quad (GI) = \frac{\text{degradotelinite} + \text{eugelinite} + \text{humodetrinite}}{\text{texto-ulminite} + \text{eu-ulminite}}$$

First a comparison was made with relative ash content (Vol % of maceral analysis) and with $\delta^{13}C$. Evaluating the diagram it was established that at more than 30 % of ash content the

$\delta^{13}C$ values varied in a relatively narrow range compare to low ash content samples. For these reasons in the next step we left the high ash content samples out of consideration. There were only three exception among high ash content samples. These samples showed similar $\delta^{13}C$ values like the next upper samples. They showed a transition to their neighbour coal facies.

Finaly we represented the correlation between GI, $\delta^{13}C$ and coal facies. By the help of using Gelification Index GI and organic stable carbon isotope ratio more detailed conditions (pH, EH) of different peat forming environments could be described. Swamp facies was below 1.0 GI and marsh facies varied between 1.0-100.0 GI. In a given coal facies exponencial connection was between GI and $\delta^{13}C$. As a result it was established that the higher is the Gelification Index and the lower the value of $\delta^{13}C$ the degree of decomposition is the larger. So at high GI and low $\delta^{13}C$ the pH was just below neutral and the peatification conditions were more or less aerobic and dry.

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Carbon and oxygen isotope ratios in carbonates deposited from hot water emerged from a well Demjén No. 42

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Key words: isotope ratio, carbonate - water system, equilibrium fractionation factors, carbonate precipitation

In 1961 a 407.5 m deep borehole (No. 42) was drilled between villages Egerszalók and Demjén. Since that time the well continuously supplies hot water. The water temperature in the well is 66 °C. The water moves gravitatiually along the slope of the surface down to the hill until it reaches a small basin. The water temperature decreases and huge amount of carbonate is precipitating along the flow path. Carbonate was sampled at various points of the flow path, the temperature was measured at each point and water samples were taken. In the carbonate - water system the oxygen isotope ratios of the carbonates were calculated using equilibrium fractionation factors which were given by Friedman and O'Neil (1977) with following equation:

$$10^3 \ln\alpha = 2.78(10^6 T^{-2}) - 2.89$$

where $10^3 \ln\alpha = \delta_{SMOW}(\text{carbonate}) - \delta_{SMOW}(\text{water})$

No agreement was found between the calculated and measured oxygen isotope ratios (Table 1., Fig. 1.) which show that the oxygen isotope of carbonate are not in equilibrium with oxygen isotopes of water. These results show that we can not expect that carbonate precipitated from various warm springs reaches equilibrium conditions with water. Therefore reconstruction of the past water temperature of the spring is not possible even the $\delta^{18}O$ value of the water is known.

The carbon isotope ratio of the carbonate as a function of temperature has a similar trend than the oxygen isotope ratios which is characteristic for kinetic isotope fractionation. The increasing tendency of $\delta^{13}C$ with decreasing temperature is explained by the fact that dissolved CO_2 is leaving continuously the bicarbonate - carbon dioxide - water - carbonate system and in the gas phase the light isotopes are enriched. Therefore the dissolved CO_2 is enriched in heavy carbon isotopes which will effect the carbon isotope ratios of the precipitated carbonate.

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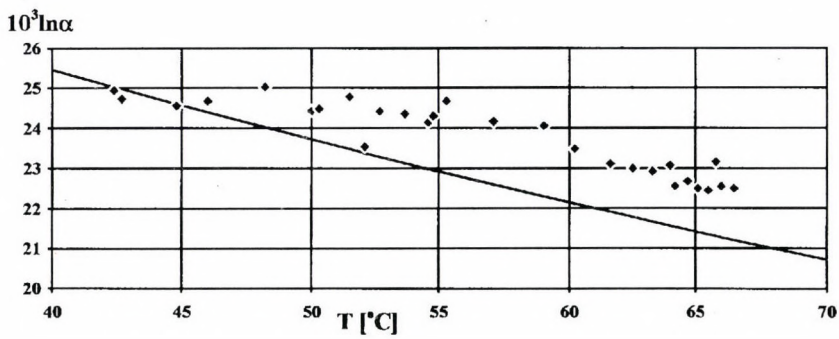
Table 1. Isotope ratios of the carbonate precipitated from water of the well Demjén No. 42. $\delta^{18}O_{SMOW}$(water) = -11,39 ‰

Carbonate samples	T [°C]	$\delta_{(SMOW)}{}^{18}O$[‰] (measured)	$\delta_{(SMOW)}{}^{18}O$[‰] (calculated)
1	66,5	11,11903	9,818031
2	66	11,17057	9,889138
3	65,8	11,76847	9,917668
4	65,5	11,0778	9,960559
5	65,1	11,11903	10,01792
6	64,7	11,29428	10,07549
7	64,2	11,18088	10,14774
8	64	11,686	10,17673
9	63,3	11,54168	10,27861
10	62,5	11,61384	10,39581
11	61,6	11,72724	10,52868
12	60,2	12,09835	10,7375
13	59	12,67563	10,91859
14	57,1	12,77872	11,20937
15	55,3	13,29415	11,48952
16	54,8	12,92304	11,56815
17	54,6	12,7581	11,59971
18	53,7	12,97458	11,74243
19	52,7	13,03643	11,90239
20	52,1	12,1602	11,99908
21	51,5	13,39723	12,09631
22	50,3	13,09828	12,29238
23	50	13,04674	12,34174
24	48,2	13,64464	12,64081
25	46	13,29415	13,01324
26	44,8	13,17044	13,21965
27	42,7	13,34569	13,58654
28	42,4	13,56217	13,63955

Fig. 1. Per mill fractionation as a function of temperature for carbonate-water system; ◆ experimental values measured for carbonate precipitated from water of the well Demjén No. 42.; — calculated values assuming equilibrium conditions



The origin of the water in Lake of Vrana

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Key words: isotopes, oxygen-18, deuterium, carbon-13, carbon-14, tritium, mean residence time, Lake of Vrana, spring.

The hydrogeological problem

The Lake of Vrana, situated in the central part of Cres Island, has, as a water phenomenon, a dominant position and significance. The size of the lake is fascinating for the islands of so elongated shapes as are the Cres and Losinj. The total area of the lake is 5km^2, maximum depth is 70 m (60 m below sea level) and it accumulates 220 million m^3 of fresh water. Such amount of entirely fresh water, concentrated at an almost entirely arid group of islands, has provoked extraordinary attention from researchers during the whole century, even if one takes into consideration the fact that the lake is the only accurate source of potable water of the entire area (Gavazzi, 1902; Cecconi, 1940; Petrik, 1969; Golubić, 1989; Biondić *et al.*, 1991; Biondić & Dukarić, 1993; Hertelendi *et al.*, 1994a; 1994b).

The basic problem of the Lake of Vrana is the origin of its water. The present exploration and plans for further explorations are aimed at solving this problem. Most of this exploration suggests the concept of the water origin from both the local and regional drainage areas. However, for the time being we still have to take into account the earlier concept of the lake water origin from only the local drainage area, i.e. from Cres Island only. These two concepts require substantially different actions in the future. If the concept of combined local and regional recharge systems is valid, those actions have to be directed toward the continental mainland, that means toward a storage of seasonal high waters and an artificial recharge of the karst underground during the dry seasons. By that way, the groundwater resource potential of the Kvarner

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karst underground will be maintained, at least in its general sense. Plans for such actions already exist.

If only the local drainage areas is concerned, substantial hydrological changes should not be expected at the lake but, anyway, the rate of total lake water pumping should be studied carefully. The existing water budget analyses show that the rate of pumping already approaches the upper admissible limit and any increase in the pumped amounts leads to the mining of water resources. The maintenance of the existing water-supply systems are feasible only under a strict control of pumping rates. In that case, the water-supply development of the group of islands considered could be achieved by linking the insular water-supply system with that one from the Kvarner mainland areas in which the available water resources are already limited.

Interpretation of the isotope results

From the strong enrichment of ^{2}H and ^{18}O (see Table 1) in the lake water (composition close to sea water) one can conclude that there does not exist any considerable outflow from the lake.

The inflow of karst water into the lake can be only of minor importance since the amount of precipitation is about the same as that of evaporation from the surface of the lake (about 1000 mm per year) and there is no considerable outflow.

From the existing isotope data there is no evidence of an inflow of karst water in the deepest part of the lake. If there exists an inflow of water which cannot be detected by isotope measurements, this can only be explained by the following mechanism: During periods with high water level in the lake, lake water is flowing into the neighboring karst water system. If the water level in the lake is below that in the karst aquifer, this water may flow back into the lake again. In this case the isotope ratios of the flowing water do not significantly differ from those of the lake water.

From the strong enrichment of ^{2}H and ^{18}O in the lake water it can be concluded that also ^{3}H becomes considerably enriched in the lake water (about 10%). If the enrichment of tritium is taken into account a mean residence time (MRT) of 30-40 years was obtained from the measured tritium values. More precise value of MRT can not be given because of the lack of systematic tritium measurements of the local

precipitation. In this calculation we used the ^{3}H data of precipitation collected in Genoa IAEA Network Station.

The MRT can be given for this lake as the ratio of annual inflow divided by the total volume of the lake. The average depth of the lake is approximately 40 m, the precipitation rate is 1 m/year. The obtained 40 year MRT is in good agreement with that of obtained from the isotope data. This suggests that the lake water originates from the local drainage area i.e. Cres Island only. Therefore the existing water supply system are feasible only under a strict control of pumping rates because water budget analyses show that the rate of pumping already approaches the upper admissible limit.

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Table 1.- Radiocarbon and tritium concentrations and isotope hydrological data as a function of depth in the Vrana Lake.

Profile/depth	$\delta\ ^{13}C$ [‰] (PDB)	$\delta\ ^{18}O$ [‰] (SMOW)	δ D [‰] (SMOW)	pMC [%]	^{3}H (TU)	Temp. °C
1/0	-1,29	-0,41	-8,55	109,5	20,8	19,5
1/10	-1,09	-0,48	-10,25	110,1	20,3	16,5
1/20	-1,42	-0,56	-9,12	109,0	21,4	13
1/30	-1,28	-0,46	-9,30	110,8	19,7	12,5
1/40	-1,71	-0,49	-9,09	110,2	18,0	10,5
1/50	-2,19	-0,56	-8,70	109,8	20,6	11
1/60	-1,69	-0,40	-9,09	107,7	20,4	10
2/0	-1,27	-0,33	-10,76	110	21,2	22
2/10	-1,28	-0,23	-9,41	109,4	20,6	16,6
2/20	-1,25	-0,22	-9,58	109,1	20,9	13
2/30	-1,06	-0,27	-9,78	110,6	23,3	11,5
2/40	-1,54	-0,39	-10,97	110,4	21,9	10,5
2/50	-2,02	-0,52	-10,03	109,4	22,0	9,5
3/0	-1,58	-0,70	-10,44	110,3	20,6	
3/10	-1,19	-0,45	-8,41	110,1	20,0	
3/20	-1,32	-0,35	-10,14	110	20,1	
3/30	-1,38	-0,45	-10,93	109,7	23,1	

RADIOCARBON AND URANIUM-SERIES DATING OF TRAVERTINE

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Keywords: travertine, radiocarbon, uranium-series dating

Introduction

Travertine or tufa, calcareous deposits precipitated from fresh water, is the result of decomposition of dissolved calcium bicarbonate in cold fresh water. The process of calcium carbonate precipitation depends on physicochemical conditions (temperature, pH, alkalinity, concentration of calcium, magnesium and dissolved CO_2 in water) as well as biological, hydrogeological and climatological conditions.

We investigated the physicochemical conditions for travertine precipitation at Plitvice Lakes area as well as isotopic measurements including ^{14}C, ^{13}C and ^{18}O in water and travertine samples (Srdoč et al, 1985). $\delta^{13}C$ values of travertine ranging from -9.6 to -8.7 ‰ confirmed the biogenic origin of travertine, which makes the radiocarbon dating of travertine samples possible.

During the precipitation of calcium carbonate from fresh water the trace amounts of uranium are incorporated in travertine. Thus, it was possible to determine the age of travertine beyond the ^{14}C range by the $^{230}Th/^{234}U$ dating. Results of ^{14}C and $^{230}Th/^{234}U$ dating are reliable if the travertine samples belong to the so called "closed system".

In this paper we present the results of radiocarbon and $^{230}Th/^{234}U$ dating of travertine samples from two karst areas in Croatia: the Plitvice Lakes and the Krka River. Both areas are situated in the Dinaric Karst region and belong to the National Parks. Recent travertine was found along streams and lakes, and its precipitation is presently very intensive, whereas old travertine deposits were found as outcropping above the present water level.

Radiocarbon dating

Two factors affected the accuracy of the ^{14}C age of travertine samples: the unknown initial ^{14}C activity (A_0) of the sediment, mainly affecting younger (Holocene) samples, and contamination of old travertine deposits with recent carbonate, making ^{14}C ages appear younger (Srdoč et al., 1986). Measurements of ^{14}C activity of dissolved inorganic carbon (DIC) in water samples from Plitvice Lakes showed the increase of ^{14}C activity from karst springs to the estuary (Srdoč et al., 1986a). The same phenomenon, which is due to ^{14}C isotope exchange between DIC and atmospheric CO_2, was also observed in the

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Krka River. Experimental values of the A_0 of travertine deposits from Plitvice Lakes increase downstream from 70 to 90 per cent of modern carbon (pMC) and for Krka River the A_0 values range from 75 to 95 pMC. The ^{14}C age of travertine samples collected at Plitvice Lakes and the Krka River area are shown in Figure 1. The results are expressed in pMC and in years BP calculated by A_0=85 pMC. Most of the surface samples of travertine in both karst areas range in age from recent to 6000-7000 years BP (Fig. 1, group A). Very good agreement in ^{14}C age of travertine samples with lake sediments and peat sediments in the same area of Plitvice Lakes (Srdoč et al., 1983; Srdoč et al 1986) confirmed that the paleoclimate conditions in this period was favorable for lake formation with travertine barriers and calcite deposits as well as for peat growth.

^{14}C measurements of old travertine outcrops in the most cases gave ^{14}C ages out or close to the lower detection limit of the method (>40000 years). A small number of old travertine samples showed ^{14}C ages from 20 000 years BP down to the lowest limit (Fig. 1, group B). Measurements of several fractions of old travertine samples showed that most of these sample were contaminated by recent carbonate (Srdoč et al., 1986).

$^{230}Th/^{234}U$ dating

Samples of old travertine outcrops with ^{14}C age out or very close to the lowest limit of the method were measured by $^{230}Th/^{234}U$ method. Chemical procedure for thorium and uranium separation and purification includes the dissolution of carbonate samples (100-150 g) in conc. HCl, coprecipitation of uranium and thorium with $Fe(OH)_3$, selective adsorption and desorption on anion exchange resins and finally electroplating. A known activity of $^{228}Th/^{232}U$ tracer is added to the solution. (Hennig et al., 1980, Ivanovich and Harmon, 1982). The α-activities of uranium (^{232}U, ^{234}U, ^{238}U) and thorium isotopes (^{228}Th, ^{230}Th, ^{232}Th) were measured by an α-spectrometer (ultra ion-implatned-silicon detector) and the α-spectra were stored in an 2000-channel analyzer. The ratio of $^{234}U/^{238}U$, $^{230}Th/^{232}Th$ and $^{230}Th/^{234}U$, the respective uranium and thorium contents as well as the $^{230}Th/^{234}U$ age are determined by a computer program (Ivanovich and Harmon, 1982).

Our $^{230}Th/^{234}U$ dating procedure was cross-checked by comparing our data on several travertine samples that were also measured by three different laboratories: Niedersächisches Landesamt für Bodenforschung, Hannover (M.A. Geyh), U.S. Geological Survey, Denver, Colorado (P.O'Malley) and Department of geology, Florida State University, Tallahassee (J.K. Osmond) (Srdoč et al., 1994). Our $^{230}Th/^{234}U$ dating of these samples was in good agreement with results obtained in these laboratories.

The results of our $^{230}Th/^{234}U$ dating of travertine from the Plitvice Lakes and Krka River areas are shown in Table 1. We dated only hard, compact, possibly crystalline form of travertine samples to avoid the contamination of sample with detrital thorium. All samples were dated also by ^{14}C method. ^{14}C and $^{230}Th/^{234}U$ ages of Holocene sample UZ-17 (Krčić) are in good agreement. Test measurements of samples from Plitvički Ljeskovac (UZ-9, 10, 12, the same

sample with three different preparation) and Krčić (UZ-21, 28, 29) showed good reproducibility of the $^{230}Th/^{234}U$ measurements. Samples UZ-8 and UZ-21 with ^{14}C age of 23.8 and 26.9 ka, respectively, indicate the contamination with recent carbonate and these ^{14}C results are not acceptable (Fig. 1, group B).

All $^{230}Th/^{234}U$ results presented at Table 1 show the age between 100 and 120 ka. This time period belongs to the Stage 5 of oxygen isotope time scale. It indicates that the formation of old travertine deposits at Plitvice Lakes and Krka Rivers area coincide with the last Riss/Würm interglacial.

Conclusion

Radiocarbon and uranium-series dating of travertine samples showed good agreement (Holocene samples) and reproducibility of the results for hard, compact, crystalline calcite. Porous travertine samples are contaminated with recent carbonate, and thorium detritus or uranium leaching is possible.

^{14}C and $^{230}Th/^{234}U$ ages of travertine samples from two karst areas in Croatia, Plitvice Lakes and Krka River areas showed that the formation of travertine deposits coincide with the warm, humid interglacial and that the process of calcium carbonate precipitation depends on climatic condition. Travertine samples from both areas belong to Holocene and Riss/Würm interglacial.

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Table 1: Results of $^{230}Th/^{234}U$ dating of travertine from the Plitvice National Park and the Krka National Park

UZ-Lab. No.	Location	Description of sample	U (ppm)	$^{234}U/^{238}U$	$^{230}Th/^{232}Th$	$^{230}Th/^{234}U$	$^{230}Th/^{234}U$ age (ka)	^{14}C age (ka, BP) (A_0=85%)
Plitvice National Park								
8	Bijela Rijeka	compact tufa	0.192	1.430±0.023	12.8±0.5	0.656±0.014	107 ± 4	23.8 ± 1
9	Plitvički Ljeskovac	hard, compact tufa	0.235	1.501±0.030	13.7±0.7	0.666±0.018	109 ± 5	>40
10			0.229	1.492±0.027	14.2±0.5	0.726±0.016	126 ± 5	
12			0.261	1.503±0.021	14.1±0.5	0.674±0.013	111 ± 4	
19	Plitvički Ljeskovac	hard, compact tufa	0.249	1.536±0.017	50.3	0.611±0.010	96 ± 3	>40
20	Plitvički Ljeskovac	hard, compact tufa	0.222	1.576±0.027	47.9	0.624±0.011	98 ± 3	>40
Krka National Park								
17	Krčić	crystalline tufa	0.224	1.425±0.014	4.9±0.3	0.056±0.002	6.3 ± 0.2	5.9 ±0.1
21	Krčić	hard, compact tufa	0.320	1.246±0.014	3.5±0.1	0.682±0.013	118 ± 6	26.9 ± 0.8
28			0.303	1.212±0.020	3.5±0.1	0.705±0.021	124 ± 9	
29			0.369	1.132±0.010	2.6±0.1	0.669±0.016	114 ± 8	
23	Krka, Quarry Topolje	hard tufa with three separate layers	0.230	3.194±0.913	4.7±0.1	1.038±0.027	U leaching	>40
24	Krka, Lake Mlinarsko	very hard, compact tufa	0.466	1.155±0.012	6.5±0.1	0.643±0.012	109 ± 4	32.5 ± 2.8

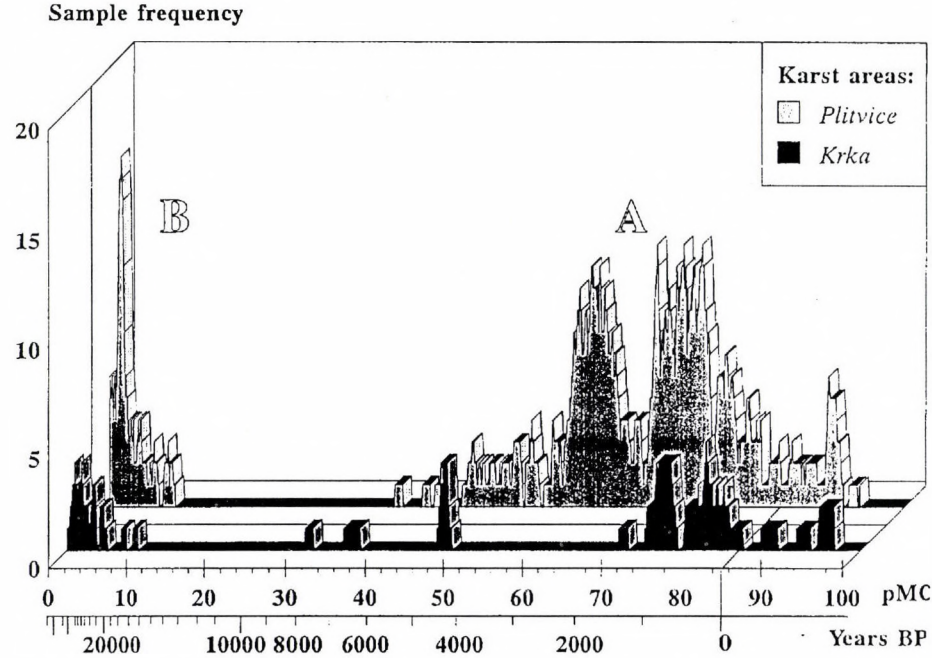

Figure 1. Frequency of ^{14}C results of travertine samples collected in the Plitvice National Park and Krka National Park. The results are expressed in pMC and in years BP (calculate by Ao = 85 pMC).

LONG-TIME ATMOSPHERIC TRITIUM RECORD IN CROATIA

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Keywords: tritium, precipitation, atmospheric water vapor, atmosphere

Introduction

The disturbance of the natural tritium concentration in the atmosphere caused by nuclear weapon tests in early sixties made atmospheric tritium as a very important tracer in environmental studies. Data of the environmental isotopes (^3H, ^2H and ^{18}O) in monthly samples of precipitation taken by a global IAEA-WMO network in the period from 1953 to 1991 have been published by the IAEA in ten volumes of the publication "Environmental Isotope Data: World Survey of Isotope Concentration in Precipitation". The data are being widely used in hydrological, hydrometeorological and climatological studies. Tritium concentration as well as stable isotope content (^2H and ^{18}O) in precipitation and the relevant meteorological data at the Zagreb station have been published in these publications since 1976 (IAEA 1983, 1988, 1989, 1994).

In this paper we present ^3H data measured in Zagreb precipitation and compare with ^3H data in Ljubljana station (Slovenia). We also measured tritium for one year period in three additional station in Croatia as well as in water vapor collected from the air in Zagreb and suburbs.

Sampling and measurement

Monthly samples of precipitation at station Zagreb (rain-gauge was situated at the Ruđer Bošković Institute) and Ljubljana have been routinely measured since 1976 and 1981, respectively. For shorter periods of time, tritium in monthly precipitation was measured at Plitvice National Park, SE from Zagreb (1980-1982), and in Rijeka, at the North Adriatic coast (1986-1987). In 1995 we started to collect precipitation samples also on Mt. Sljeme, at ~1000 m a.s.l., nearby the city of Zagreb.

Collection of atmospheric water vapor started at the Ruđer Bošković Institute, Zagreb, and at several sampling sites in Zagreb area in 1988, with the aim of studying possible local tritium contamination. Weekly samples of air moisture were collected by pumping air through a silicagel trap followed by desorption of water at 350°C . Water samples were converted to methane which is used as a counting gas in proportional counter. Methane was obtained by reaction of water samples with aluminium carbide at 150°C (Horvatinčić, 1980).

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Results and discussion

The record of ^{3}H data in Zagreb station in the period of 1976 to 1994 is statistically elaborated in Fig.1. Yearly mean values of Zagreb precipitation decrease from 10.1 Bq/L in 1976 to 0.5 Bq/L in 1994, and the decrease can be well described by the exponential decay curve (full line, Fig. 1). The values of maximal and the minimal activities in monthly precipitation during the year decrease following again approximately exponential decay. The lowest value, measured mainly in the winter time, in the last three years is 0.5 Bq/L, very close to the assumed natural pre-bomb tritium activities. The maximal values, measured mainly in summer period, are between 2 and 5 Bq/L. The values of max/min ratio fluctuate between 2 and 5 with an exemption in 1977 with the value of 9.

Tritium concentration in precipitation at three continental station (Zagreb, Ljubljana and Plitvice) closely follows each other showing seasonal changes typical for the Northern hemisphere (I. Krajcar Bronić et al., 1992). At the Adriatic coast (Rijeka station) tritium concentration is, on the average, half of that at Zagreb. It is closely correlated to Genoa, the nearest Mediterranean station of the IAEA/WMO network. Figure 2 shows comparison of tritium concentration in precipitation at Zagreb and Ljubljana in the period from 1988 to 1994 and at Mt. Sljeme in 1995. Significant increase of tritium concentration in Zagreb precipitation in 1994 and 1995 comparing with that in Ljubljana and Sljeme precipitation is observed. It indicates the local contamination at the Ruđer Bošković Institute during the last two years due to the use of gas and liquid compounds rich in tritium. These results are not acceptable for the global network. Samples of precipitation collected at the Mt. Sljeme will be used for the future network for Zagreb station.

Local contamination by tritium at the Ruđer Bošković Institute was also indicated in atmospheric water vapor. Tritium activity of weekly samples of atmospheric water vapor collected at the Ruđer Bošković Institute from 1988 to 1995 is shown in Figure 3. The results show that tritium concentration in atmospheric water vapor is several times higher than in precipitation from the same period. At other investigated sites in Zagreb area the tritium concentration in water vapor was 0.02 to 0.04 Bq/m^3 which is very close to that in precipitation and no local contamination similar to that at the Institute (0.07-4.42 Bq/m^3) was observed. Higher tritium concentration in Zagreb precipitation in 1994 and 1995 corresponds to significant increase of tritium in atmospheric water vapor.

Conclusion

Our systematic monitoring of atmospheric tritium has shown that it should consist of continuous monitoring of tritium in both precipitation and atmospheric water vapor. Tritium in precipitation reflects mostly global changes in the atmosphere, although it can be influenced by the local contamination. Tritium concentration in atmospheric water vapor is very sensitive to local sources of tritium and it is a good indicator for local contamination. Sampling

site for monitoring of the natural tritium in atmosphere using for network should be carefully chosen.

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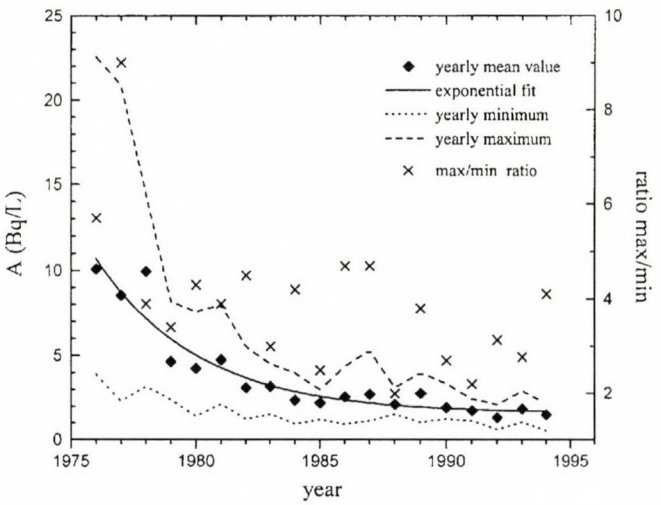

Figure 1. Statistically elaborated tritium data of precipitation at Zagreb station in the period from 1976 to 1994.

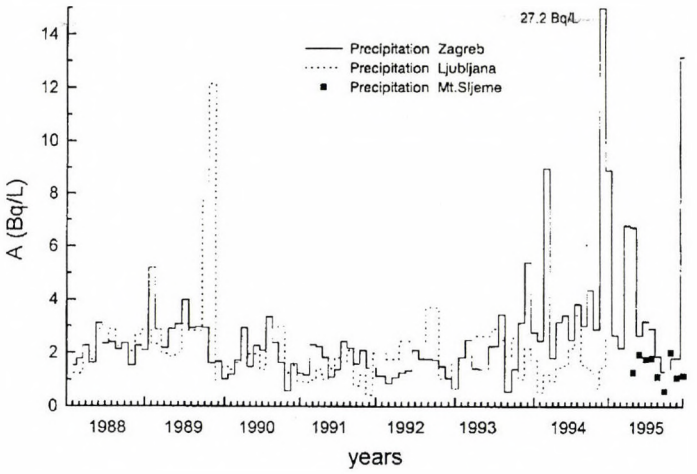

Figure 2. Tritium concentration in precipitation at Zagreb, Ljubljana and Mt. Sljeme station in the period from 1988 to 1995.

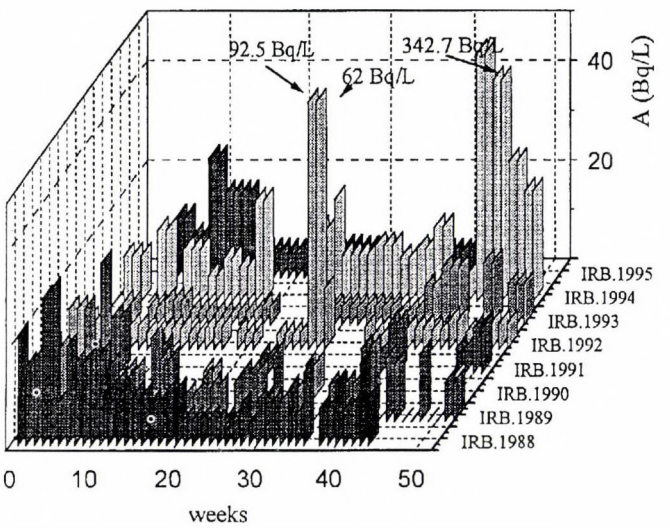

Figure 3. Tritium concentration in atmospheric water vapor measured in weekly samples at the Ruđer Bošković Institute in the period from 1988 to 1995.

$\delta^{13}C$ and $\delta^{34}S$ in PEAT PROFILES as a POSSIBLE RECORD of GLOBAL CHANGES

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Sulphur and carbon isotope analysis (Fig.1&2) and organic sulphur concentration measurements have been carried out in two peat profiles from peat-bogs in Sudety Mts., SW Poland (Zieleniec and Szrenica) and three peat profiles from lowlands of Southern Thailand (Bacho I & II and To Daeng). These profiles represent approximately the last two Millennia

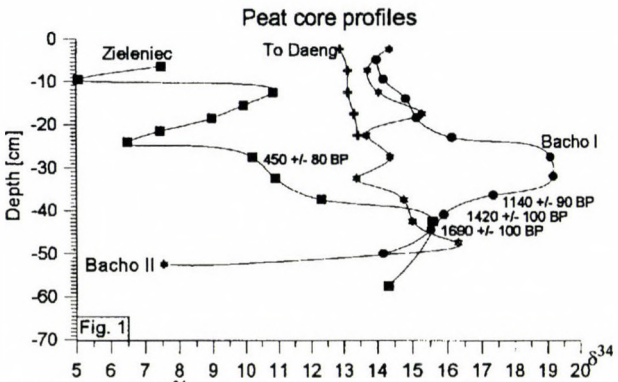

Fig. 1. Vertical variation in the $\delta^{34}S$ value in the peat profiles from Poland (Zieleniec i Szrenica) and Thailand (To Daeng and Bacho I & II).

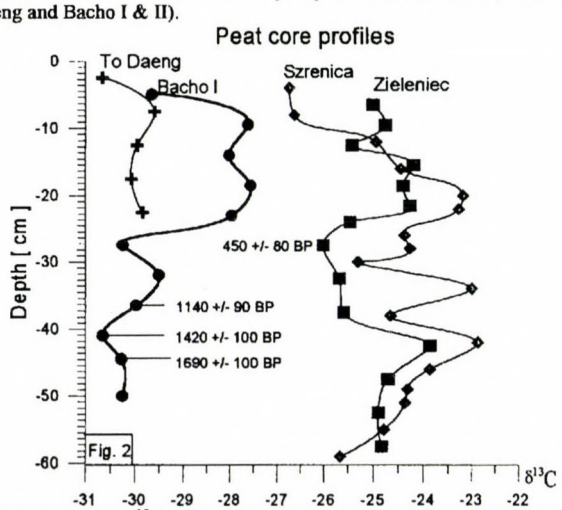

Fig. 2. Vertical variation in the $\delta^{13}C$ value in the peat profiles from Poland (Zieleniec i Szrenica) and Thailand (To Daeng and Bacho I).

It seems that the main factor controlling carbon isotope ratio in peat are predominantly temperature and perhaps the water level on the peat bog. The main factor controlling organic sulphur isotope ratio in peat is water level. In general, all the profiles examined show coincidence in the carbon isotope variations in time. It may prove that global climatic variations are recorded in the carbon isotope composition of peat. In the youngermost levels of the peat, a distinct shift of the $\delta^{13}C$ into the negative direction may be resulted by an increase in atmospheric carbon dioxide coming from fossil fuel combustion. The $\delta^{13}C$ and $\delta^{34}S$ variations evidence that climate cycles may vary with time in a matter of less than 100 years.

Due to significant increase in $\delta^{34}S$ value in the peat representing approximately the time from VI to XII century, (Fig. 1) one may suggest that in this time a local increase of the sea level, in the SE Thailand, took place.

The $\delta^{13}C$-$\delta^{34}S$ plot (Fig.3) show that the lower part of the Zieleniec profile represents shallow lake vegetation and sedimentation and the upper part represents typical high peat bog conditions.

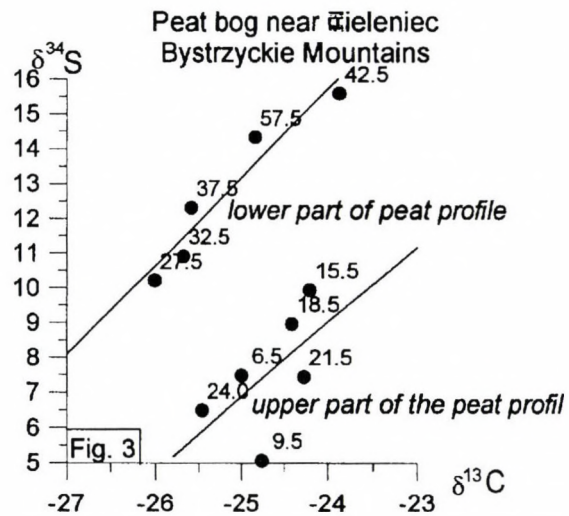

Fig. 3. $\delta^{13}C$-$\delta^{34}S$ correlation for lower and upper part of the Zieleniec profile. Numeric labels show depth in the profiles in centimetres below surface. Open circle - sample from upper part in the group of the lower part of the profile.

In contrast to the older part of the Zieleniec peat profile, since XV/XVI century (beginning of the Little Ice Age), the carbon isotope record vary coincidentally with the temperature record (Fig. 4) for England. It may suggest that an unification of atmospheric circulation and climatic variations in the Central and Western Europe have taken place after XV century.

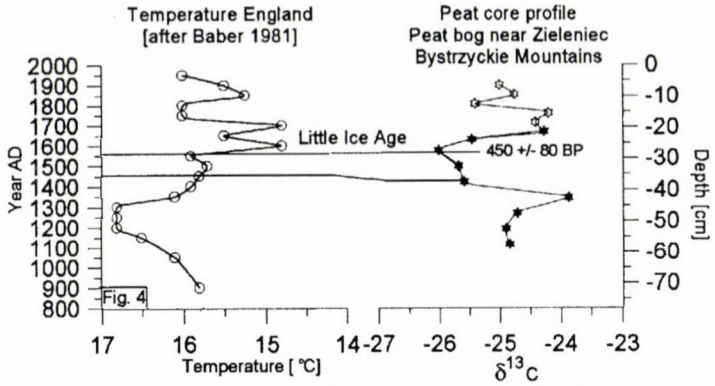

Fig. 4. Temperature variations estimated from historical and biological data for lowlands in England [after 20] compared to corresponding $\delta^{13}C$ variation in the Zieleniec peat profile.

POSSIBLE VARIATIONS in the MECHANISMS of METHANOGENESIS in VARIOUS TROPICAL FRESHWATER SEDIMENTS

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The observations concerned methane from wetlands in Southern Thailand. Diurnal variations in the $^{13}C/^{12}C$ ratio in bubble methane [1] formed in shallow-water sediments were observed at a pit (c.a. 50 m^2, 2 m deep, sulphate-rich artificial pond), a pond (c.a. 0.1 km^2, rich in submerged and emergent plants), and a canal (isolated from the ground by an impermeable cement cover, c.a. 50 cm deep and 1 m wide). Sampling was made on 5 and 6 September 1994. Vertical distribution of isotope composition of methane in sediments [2] was observed in To Daeng tropical forest sediments.

The isotope data show that $\delta^{13}C$ of methane was the lowest in the night and the highest in the morning, ranging from -64 to -46‰ (Fig. 1). Smaller values were supposedly resulted from an enhanced activity of the CO_2-reducing pathway of methanogenesis. Higher values, on the other hand, were presumably due to reduction of CO_2 pool size which should have increased the relative contribution of the acetic acid pathway. Also, primary production that increased daytime should have consumed isotopically lighter CO_2 leaving behind heavier CO_2 in the residual CO_2 pool. The canal methane showed low $\delta^{13}C$, presumably due to low activity in the primary production. The pond methane showed relatively small diurnal variation, presumably because the light penetration into water was limited by both high turbidity and abundant macrophytes. This could be the reason of the significant shift in phase in the minimal $\delta^{13}C$ value from night to early morning and the maximal $\delta^{13}C$ value from sunset time to early night. The pit methane showed relatively high $\delta^{13}C$, possibly due to bacterial oxidation of methane, especially in the very end of the night.

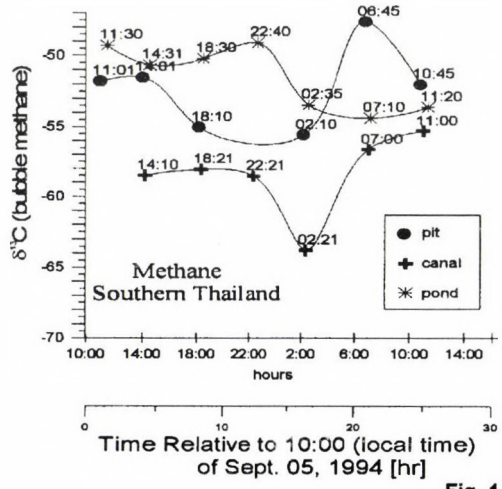

Fig. 1

In the freshwater To Daeng sediments, visually judged methane production decreased with increasing depth in sediments and gradually ceased at a depth of about 80cm. Likewise, gradual decrease of $\delta^{13}C$ (Fig. 2) suggests that the CO_2-H_2 pathway become more important with increasing depth in sediments, and methanogenesis via acetic acid fermentation decreased with increasing depth in sediments.

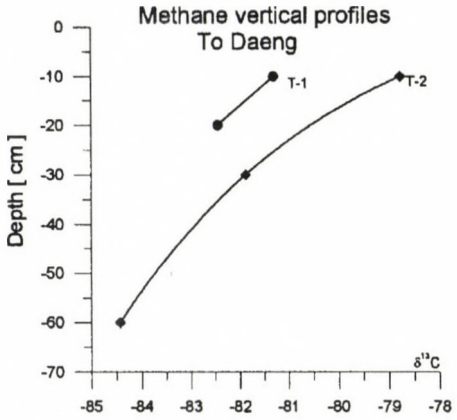

Fig. 2

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Isotopic composition of atmospheric methane in Cracow

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Keywords : methane, greenhouse effect, isotopic composition, methane concentration,

Methane is an important component of the atmospheric photochemistry and the climate system. It has been shown that the concentration of methane is increasing at about 1 % per year in the Earth's atmosphere [Khalil & Rasmussen, 1990]. The concentrations of methane in the old and ancient atmospheres can be deduced by analysing air bubbles buried long ago in polar ice [Craig & Chou, 1982, Chappellaz et al.,1990]. The present concentration of methane -1.72 ppmv may be more than twice as high as the natural levels of Industrial Revolution,150 years ago.

It is well known that all methane sources are located on the Earth's surface and that the main methane sinks are located in the atmosphere. There are natural and anthropogenic methane sources. The main anthropogenic methane sources are ruminants, coal mining, natural gas from gas wells, burning of fuels, rice paddies, organic wastes and gas leakages from city gas network [Stevens & Engelkemeir, 1988].The isotope variations in methane can provide information about its sources. The carbon isotopes can be used as a finger printing technique to determine the relative strengths of various atmospheric methane sources by their isotopic signatures.

The separation of the CH_4 from air and conversion to CO_2 for isotopic analysis was carried out by the method of Stevens and Rust [Stevens & Rust,1982, Lowe et al.,1991]. The air sample is metered into a high-vacuum extraction line through a series of highly efficient liquid nitrogen traps to remove H_2O, CO_2 and N_2O. The air then passes through a bed of Schutze's reagent to quantitatively oxidise CO to CO_2, which is subsequently trapped cryogenically. Methane is combusted over platinized silica at 750°C and the resulting CO_2 is cryogenically trapped and the ratio of $\delta^{13}C$ is determined for the converted CO_2.

Quasi continuos observations of the isotopic composition of atmospheric methane in Cracow were made from March 1995 to July 1995. These data are used to get information on methane sources inside the Cracow area. From the correlation of the isotopic composition of atmospheric methane and its inverse concentration we can calculate the isotopic composition of the mean methane source [Thom et al,1993] [Fig.1].

The mean isotopic composition of the methane source in Cracow area $\delta^{13}C_{SOURCE}$= -54.86 ‰ has nearly the same isotopic composition as the methane from city gas network $\delta^{13}C$= - 54.52 ‰. We can assume that methane leakages from city gas network is the main anthropogenic methane source observed in Cracow area [Fig.2].

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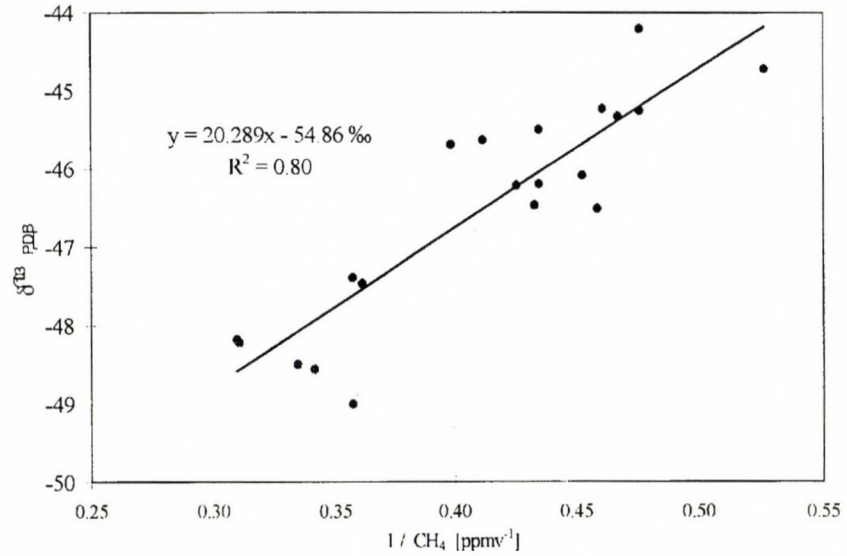

Fig.1 Correlation of $\delta^{13}C$ of atmospheric methane in Cracow with its inverse correlation. From the isotope intercepts of the regression line ($1/CH_4=0$) we derive the isotopic composition of mean methane sources inside the Cracow area.

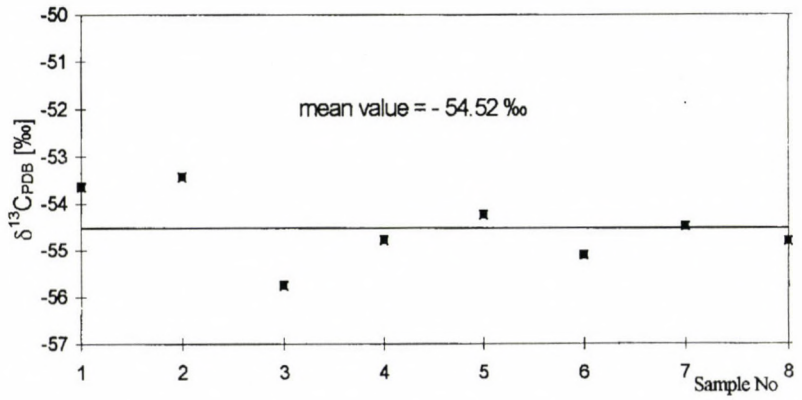

Fig.2. Results of $\delta^{13}C$ of methane from city gas network.

ISOTOPE GROUND-WATER INVESTIGATION OF A CRETACEOUS BASIN IN THE BOHEMIAN MASSIF

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Abstract

During the hydrogeological investigation of the basin of Police nad Metují in north-east Bohemia (Czech Republic), isotope techniques were used to clarify the ground-water flow system. The basin consists of a sequence of Upper Cretaceous sediments. It is tectonically separated from the main Cretacous basin of northern Bohemia at its north-eastern margin.

The area of the Police nad Metují Basin on the Czech territory is about 200 km^2. Its surface is at altitudes mainly between 450 and 550 m a.s.l. but along its margins it reaches more than 800 m a.s.l. The lowest point 390 m a.s.l. is in its southern part where the river Metuje leaves the basin. The mean discharge of this river is 2.7 $m^3.s^{-1}$. The basin is almost symmetrical and elongated in NW-SE direction. The majority of strata which are Cenomanian up to Coniacian in age are sandstones, often very pure. They form two main aquifers in the Cenomanian and uppermost Turonian and Coniacian separated with marly aquicludes. The lower aquifer is confined while the uppermost aquifer in pure sandstones is unconfined. A third minor aquifer occurs within the Turonian aquiclude depending on the lithofacial development.

The piezometric level indicates natural drainage of the aquifers in the inner parts of the basin. Local groundwater flow and drainage are influenced by the tectonic dissection of the cretaceous strata and erosional dissection of the surface.

The Police Basin has been intensively hydrogeologically investigated due to its important groundwater resources. Numerous wells were drilled in the past. Some are as much as 360 m deep. They are used for public water supply. Numerous natural springs occur, some of them being affected by abstracting groundwater in wells. Samples for isotope analyses were taken from wells and springs located in the central part of the basin as well as at its margins.

Isotope techniques were used to determine whether the basin has a uniform flow system from the margins to the central part as a uniform artesian basin.

The isotope data from the Police nad Metují Basin indicate Holocene ground-water ages. Tritium in the majority of samples indicates an intensive mixing of different ground-water components with modern water of shallow origin due to the tectonic interconnection of the fissured aquifers in the morphologically dissected and uplifted region. The lowest radiocarbon concentrations and highest ground-water residence times were observed in the south-central part of the basin but no uniform ground-water flow system could be determined. The reason seems to be the tectonic dissection of the basinal structure and the morphological dissection of the surface.

Summary of the first carbon isotope studies in the East Baltic Silurian.

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Key words: carbon isotopes, Silurian, Baltic area, bioevents.

Carbon isotope studies in Phanerozoic were summarized by Holser et al.(1995). Most detailed work in Lower Palaeozoic was performed by Brenchley et al. (1995) in the uppermost Ordovician. Our studies embrace carbon isotope excursions in the whole East Baltic Silurian. Until now 8 borehole sections have been studied, but the results are only partly prepared for publication (Kaljo, Kiipli and Martma, in press). The sections represent different parts of the Silurian and the same stratigraphical intervals show similar carbon isotope excursion patterns. Some differences observed might be explained by geological reasons (gaps in the section).For dating the peaks and lows of the carbon isotope excursion detailed biostratigraphical data were used (graptolites in particular).

In the following we would like to present some results obtained from the study of the Ohesaare and Priekule borehole sections.

The Ohesaare borehole, in the northern part of the Silurian Baltic Gulf, penetrates shallow and deep shelf marlstones, limestones and dolostones. The Priekule borehole in the deep shelf belt of the basin is through marlstones and graptolitic mudstones. Most of the successions (except the upper part) are characterized by a high Sr/Ca ratio, close to marine calcites, suggesting good preservation of carbonate material. Conodont alteration indices are low (1-2). Carbon isotopes were measured in whole-rock samples. In the Ohesaare core section two distinctive $\delta^{13}C$ positive excursions were established - one in the early Wenlock *riccartonensis* and low *rigidus-ellesae* standard graptolite zones (+4.2‰) and the second in the late Wenlock *nassa* Zone (+4.6‰). Before and after the latter there are also intervals with low $\delta^{13}C$, the first just above the *lundgreni* Zone (-1.8‰) and another in the *ludensis* (perhaps reaching into *nilssoni*) Zone (-3.8‰). In the Priekule section the early Wenlock $\delta^{13}C$ peak is well represented (+3.1‰), but in the late Wenlock-early Ludlow $\delta^{13}C$ values show little variation (from 2.0 to -1‰). In this section a high peak of $\delta^{13}C$ values (+5.9‰) was determined in the Nova Beds (correlated with the topmost Gorstian and lowermost Ludfordian, Ludlow).

In drawing conclusions from the above data, we note that all three isotope events observed in the core sections occur close to the levels of important bioevents (Kaljo et al. 1995). The early Sheinwoodian Ireviken Event is followed immediately by a positive $\delta^{13}C$ peak, the early Homerian *lundgreni* Event is followed by a clear negative shift, which in turn is succeeded by a strong positive and continuing deep negative excursion. The early Ludfordian isotope Event seems to occur somewhere close to the *leintwardinensis* bioevent level. These data show a more diversified pattern of relationships between bioevents and carbon isotope excursions than recorded in some well-known

examples from around the Permian-Triassic and Cretaceous- Tertiary boundaries, where mass extinctions were followed by $\delta^{13}C$ minima due to the decline of biodiversity and bioproductivity (Magaritz, 1989).

The global sea-level curve correlated with bioevents demonstrates that most of the events occurred during shallowing phases; only the mid-Ludfordian Event coincided with an episode of sea-level rise.

Climatically, the early Sheinwoodian Event was possibly connected with a glaciation event at the Llandovery-Wenlock boundary (Grahn & Caputo, 1992), when the Snipklint Primo Episode (cooler, humid, high biodiversity and bioproduction) was replaced through the Ireviken Event by the Vattenfallet Secundo Episode (warmer, dry, low diversity) (Aldridge et al., 1993).

Interpreting the Ludlow carbon isotope excursions in the East Baltic we see in general the same kind of events more or less correlated with the positive shift in the $\delta^{13}C$ values as above, i.e. an early Ludfordian bioevent, change in ocean state, and we have repeated in most cases the observations of Jux & Steuber (1992) relating to a correlation between sea- level change and the carbon isotope excursion.

The $\delta^{13}C$ curves, environmental and biodiversity changes discussed above show some similarity to those occurring in the latest Ordovician, which were thoroughly analysed by Brenchley et al. (1995). Unlike the Ordovician changes, the Silurian glaciations are not yet firmly proved. This can be accomplished only by the study based on good oxygen data.

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A laboratory experiment to demonstrate the change of the carbon isotope ratio of deep-seated carbon dioxide while ascending to the crust's surface

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Keywords: carbon isotope ratio, deep-seated CO_2, Carpathian Basin, isotope chemistry, water-CO_2-limestone system.

In the course of an extensive research to elucidate the origin of the deep-seated carbon dioxide appearing at the crust's surface in the Carpathian Basin we have measured the $\delta^{13}C$ value of over 150 samples, collected in Hungary, Slovakia and Transylvania (Romania), covering all regions rich in CO_2 occurrences inside the Basin.

The statistical evaluation of the data resulted in a quasi-normal distribution with a maximum near to the $\delta^{13}C$= -6.5 ‰ value. The deviation from the normality is the skewed slope on the right side extending to small positive $\delta^{13}C$ data (Cornides and Kecskés, 1982, 1987).

We interpreted this distribution by suggesting the mantle origin of the carbon dioxide and the less negative (or even small positive) values appear owing to admixture of limestone CO_2, what can be expected for instance in north-eastern areas of Slovakia (Kecskés et al., 1981)

For long time our suggestion was refused by several researchers (e.g. Kertay, 1967, Barnes and O'Neil, 1976, Lesniak, 1985), and was generally accepted only after our helium isotope investigation of several carbon dioxide occurrences (Cornides et al., 1986). The presence of mantle helium at the crust's surface in the Carpathian Basin was very soon proven by another research group too (O'Nions et al., 1989).

The present laboratory investigation was carried out to demonstrate the change of the carbon isotope ratio of the CO_2 gas in the water reservoir formed by limestone rock. This is the case of the usual TDC-sampling.

The experimental set up is shown schematically in Fig. 1. The tank-CO_2 bubbled continuously through the water in the vessel simulating a mineral water source in a limestone bed. The pH and the temperature were regularly controlled. The pH-meter indicated that the chemical equilibrium was established within about twelve hours, while the isotopic equilibrium within about three weeks. During this time the carbon isotope ratio changed by 4 ‰. Unfortunately the tank- CO_2 is very different from the mantle carbon dioxide: its $\delta^{13}C$ value is also negative, but near to -50 ‰. For this reason the result of this experiment is only semi-quantitatively relevant for the genuine situation. The change of the $\delta^{13}C$ values in positive direction is, however, obvious, and its order is also reasonable.

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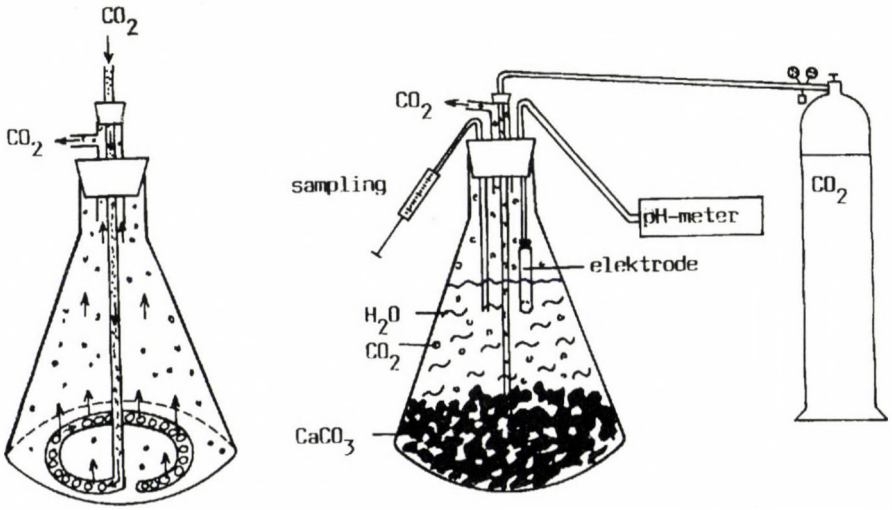

Fig. 1

$^{87}Sr/^{86}Sr$ in some mollusc shells from the Central Paratethian Tertiary sediments

J. KRÁĽ[1], I. BARÁTH[2], K. FORDINÁL[1] and G. ZIELINSKI[3]

The general increase of $^{87}Sr/^{86}Sr$ in ocean water with time due to radioactive decay of ^{87}Rb to ^{87}Sr in the rocks of the Earth's crust was predicted by Wickman (1948). This increase should be a result of an input of strontium from different geochemical sources derived by weathering and its mixing in ocean water. As Sr isotope ratio in seawater is believed to be uniform at any given time, the age of such sediments could be estimated on the basis of $^{87}Sr/^{86}Sr$ changes in carbonate marine sediments in which Sr coprecipitates with Ca. However, the reality showed to be much more complex.

Burke et al. (1982) precisely determined the curve of Sr isotope ratio changes in marine carbonate sediments and fossils of the known age from the Cambrian to the Recent. The curve of seawater $^{87}Sr/^{86}Sr$ ratio vs time exhibits a complex structure with many episodes of increasing and decreasing values. This curve represented a basis for developing of SIS - strontium isotope stratigraphy. Recently, a great effort was concentrated upon the precise calibration of $^{87}Sr/^{86}Sr$ vs age in the Oligocene and the Miocene fossils (e.g. Oslick et al. 1994).

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We analysed $^{87}Sr/^{86}Sr$ in some marine mollusc shells from the Central Paratethian sediments to check their compatibility with the existing chronostratigraphical scale (Vass et al. 1987). Moreover, we defined Sr isotopic composition in some brackish shells in order to demonstrate the difference between marine and brackish water of the same age.

Strontium for isotope measurement was separated by standard chemical procedure. Sr isotopic composition was measured in dynamic multicollector mode on VG Sector 54 along with SRM 987. The results are summarised in Fig. 1. The external reproducibility of the data may be estimated better than $30x10^{-6}$. The chronostratigrafic stages for the Central Paratethys (the left side of the graphs) are used according to Vass et al. (1987). Arrows indicate the expected biostratigrafic position of the samples. Generally, there is a good fit between SIS calibration (Oslick et al. 1994) and used chronostratigraphy.

In brackish fossils from the Upper Sarmatian sediments (with salinity about 15- 20 $^{O}/_{OO}$) $^{87}Sr/^{86}Sr$ is significantly lower ($-251x10^{-6}$) than expected for the Upper Sarmatian seawater (0.70888). As resulted from the single mixing model, the Sr riverine input must have been higher then today with low $^{87}Sr/^{86}Sr$ which could have been probably caused by volcanic activity (Kráľ et al. 1995), geochronologically well documented in that time. In contrast, the shell from the Upper Pannonian (salinity 0.5 - 3 $^{O}/_{OO}$) has $^{87}Sr/^{86}Sr$ higher ($+320x10^{-6}$) than estimated for the late Miocene ocean.

These preliminary results can be summarized as follows:

- generally, there is an agreement between the numeric age SIS calibration after Oslick et al. (1994) and the chronostratigraphy used in the Central Paratethys. The usefullness of the method in stratigraphy is enhanced by the fact that SIS is not confined to paleontologically defined species. Moreover, the method can exactly help in the direct stratigraphic correlation;
- $^{87}Sr/^{86}Sr$ from brackish shells dated biostratigraphically represents a significant geochemical information applicable in studies on various aspects of the geochemical development of the Tertiary basins and the adjacent areas.

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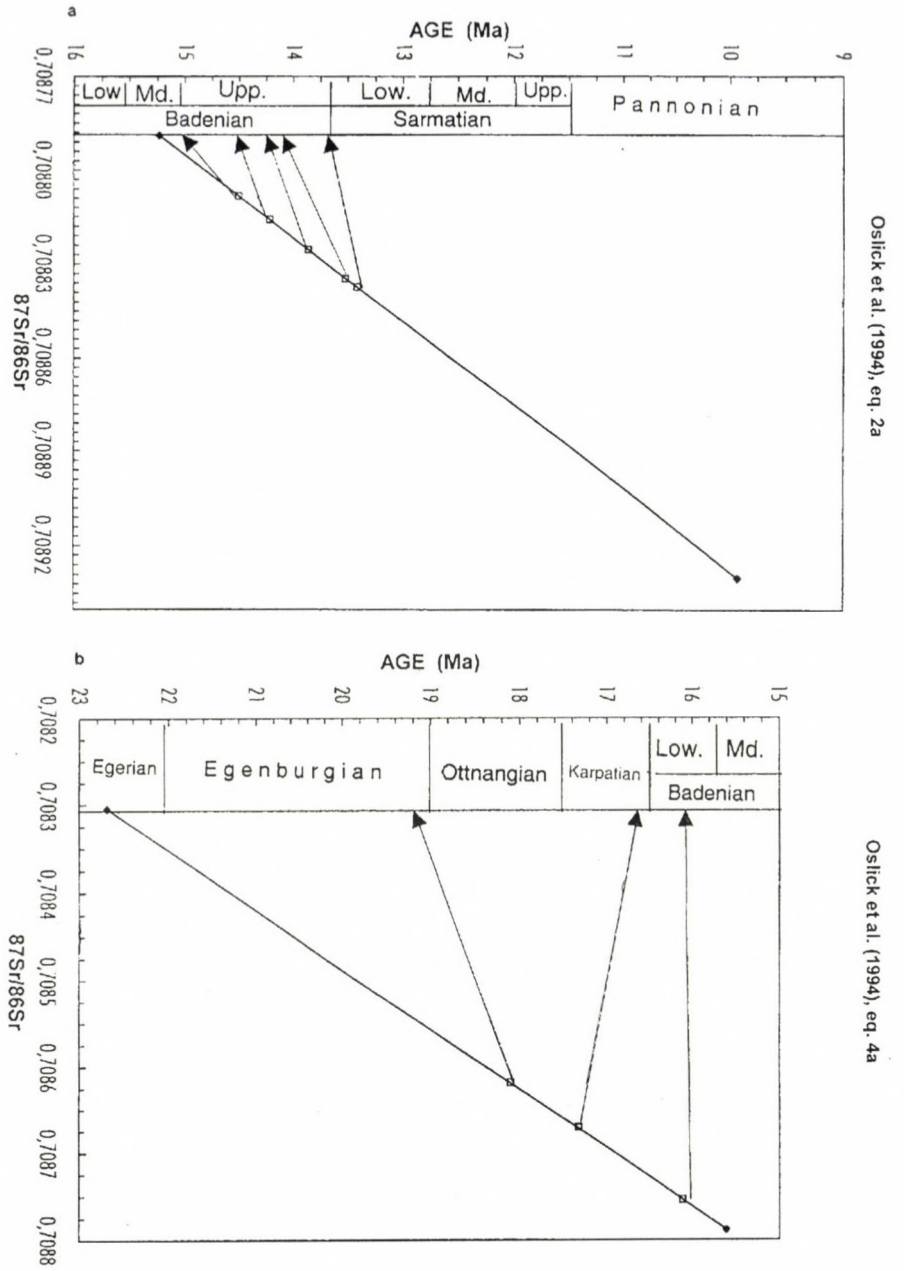

Fig. 1: The position of the analyzed shells in the calibration lines for the Neogene strontium stratigraphy, according to Oslick et al. (1994). Expected biostratigraphic positions of the samples are indicated by arrows. The external reproducibility of the measurements is estimated to be less than $30*10^{-6}$.
a) the calibration line for ages between 15.2 - 9.9 Ma.
b) the calibration line for ages between 22.8 - 15.5 Ma.

Geochemical and Stable Isotope Evidence for the Evolution of Ore-Forming Fluids in South Pamir.

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Key words: stable isotopes, tin-tungsten deposits, ore-magmatic system, voletile-rich.

Tin, tin-tungsten mineralization are known for all structure tectonic zones of South Pamir, but more signicant ore deposits is associated with the granite intrusions different geochemical types within the area development of Cretaceous granitoid magmatism. The more entire row of tin-bearing parageneses is associated with two-micaceous leucogranites of differentiated hypabyssal intrusion, where zinnwaldite-protolithionite differences of lithium fluorite granites predominate in vien phase. According to composition of the accessories leucogranites belong to monazite-ilmenite series; they rupture the granodiorites, wich have magnetite-sphene-orthite composition of the accesories. Indicator ratio values for the leucogranites are K/Rb<80; Rb/Sr>20; U/Th~0.9; for the granodiorites: > 140; < 0.6; 0.4, respectively.

Salynity of fluids from the longevity ore-magmatic system are resposible for the formation of topaz-muscovite, quartz-muscovite, aposkarn greisens with cassiterite; cassiterite-quartz, wolframite-quartz; cassiterite-sulphide ores with colloform cassiterite - is varied in a range of 7.5 -11 weight percent NaCl, T_{hom} > 420°C to 46 ones and dropping to 2,5, T_{hom}=150°C in the lode fluorite.

The calculated isotope composition H_2O in the tin-tungsten ore-forming fluids doesn't deviate from the accepted magmatic values and a contribution of meteoritic water is identified only in fluids from the low-temperature parageneses. For the most isotopically studied (and depositing at the equilibrium conditions $\delta^{34}S_{fl}$--2,0 ‰ at about 350°C) tin and tin-tungsten ores of Bazardara district (Krasnozhyna et al, 1988), the

isotopic composition sulfur from sulfides co-existing with cassiterite deviates on 3-4 per mil from -0,6 ‰ in quartz-greizen ores to -4,4 ‰ in aposkarnic metasomatites and is controled by fixed gradients of pH (3 - 3,5 values), by lg fO_2 (-28-:-31), by lg fS_2 (-8.8 -:- 9.2), and pressure within area of ore deposition. The calculated isotopic composition of water from fluids varies from 4.6 to 3.8 per mil (Krasnozhyna, 1984). Hydrogen isotopic composition from the fluid in inclusions in cassiterite, quartz, wolframite are varied in set between topaz greisens and quartz veines as follows: -40 -:- -90 per mil at 420° - 340°C. F/Cl ratio in the inclusions varies for the same assosiations from 15 to 0.8, isotopic composition of arsenopyrite from topaz greisens is - 0.4 per mil and decreases to - 1.8‰ for quartz veins. Obtained trends of the variations for deuterium, sulfur, fluorine from supercritical fluids is preferably explained of mechanism of degassing (according to B.Taylor, 1986) and suggests that the studied high-temperature facies of greisens were formed of the first separated vapor enriched besides HF also high-volatile compounds of fluorine with silicates and metals. Following portions of fluid produced by crystallizing intruzive were depleted of deuterium according to Rayleigh distillation model.

Cassiterite-stannite ores from the deposit is localized over closed dome of granitoids withih the field of metamorphic rocks are characterized by more stable isotope ratio. The first stage ores are quartz-cassiterite with localy developed, quartz - albite - k-feldspar - turmaline metasomatites for which the $\delta^{18}O_{cs}$ values ranged from 3.2 to 3.9 per mil, $\delta^{18}O_Q$ from 12 to 13 per mil, $\delta^{34}S_{PY}$ from 0.4 no 1.5 per mil. The second stage ores are cassiterite - stannite with synore quartz - sericite - chlorite - calcite metasomatites ($\delta^{18}O_{cs}$ value is + 2.6, $\delta^{18}O_Q$ ranged from 12.3 to 13, $\delta^{34}S_{PY}$ value from - 0.3 to -1.8, $\delta^{34}S_{stn}$ - 1.2) per mil, were deposited under disequilibrium conditions (in terms of isotope-sulfur systematics). Established distinction is explained by prevalence various mechanisms of ore deposition. Quartz - cassiterite ores deposited at the interaction between the deep fluorine-bearing chloride fluid and boron-bearing pore one from containing rocks at about 340°C. Quartz - stannite parageneses were presipitated at the initial stage of boiling of later

portion of the solutions saturated by the sulfur compounds at about 290°C. As a result of devolatization of acid gases the oxidizing level of fluids and pH regime were increased that is due to $\delta^{34}S$ depletation in fluids and to disequilibrium relations for the fluid - mineral system.

Gold-tungsten deposit with rare-earth-rare-metal mineralization localized in propylitize Paleogene volcanites of bazalt-rhyolith series is intruded as the minor intrusions of monzodiorite, as granitoid massifs of J-type. Ore bodies of deposit are extending cross-cutting pyrrhotite veins, rarer pyrite-pyrrhotite stockworks with disseminated scheelite, arsenopyrite, minerals of copper bismuth, etc. Gold is fine-impregnated and in the microinclutions also. Within the ore field under preferable development of actinolite-epidote-biotite association it was determined the series of heterotemperature facies of propylites from orthite-apatite-actinolite with rare-earth mineralization to beresite and multicomponent compositions reducing from outside to inner zones of the metasomatic cores. In composition of synore metasomatites of the different zones it was determined the mineral associations as the followings: K-feldspar, albite-feldspar; scapolite; tourmaline-muscovite; quartz-albite-sericite-ankerite and their variations.

Sulphur isotope composition of sulphides is similar to those both for granites of I-type and arc andesites, and varies in set 5 to 12 ‰, approaching to the equilibrium values in couple po, py - sph at about 320° - 290°C for some zones and deviating in other regardless of the composition of pH-buffer mineral associations. Single identifications of $\delta^{18}O$ values for scheelite is 3.8 to 4.5‰ (at T_{hom} for primary-secondery inclusions of 330°C) show the significant contribution of magmatic fluid.

The interaction between equilibrium with the rock of early fluid and magmatic fluids is entered by the portions in succession, agressive at the lower temperatures has determined the appearence of synore metasomatites distinct facies of acidity and the reverse vertical mineral and geochemical zonality within the ore field.

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GENETIC IMPLICATIONS OF Nd AND Sr ISOTOPIC DATA TO THE WOLFRAMITE OCCURENCES FROM PRIMORIE (FAR EAST, RUSSIA).

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Keywords: isotope, neodymium, strontium, wolframite, deposit

One of the most important aims of ore geology is the investigation of the processes of ore deposits formation. This knowledge helps in search of new deposits and in the estimation of already known ones. The formation of ore deposits is complicated multicompanent natural process the course of which depends on thermodynamic parameters (p, t, composition) of mobile ore-generating phase (fluid, hydrothermal solution, magma) and host media and on the time during which the active interaction between these components takes place.

Recently to solve the problem of oregenesis some isotope methods, particularly Sm-Nd, Rb-Sr, are used. They allow to get some data about the sequence of the ore formation processes, the source of ore-generating fluid, the source of ore component and its connection with the host rocks. Also these methods are used to determine the age of ore deposit and particularly according wolframite and scheelite.

In the present work under investigation there were wolframite-cassiterite-rare-metal ore deposit Zabytoe and wolframite-scheelite-sulfide ore deposit Rudnoe situated in the zone of the main synclinorium of Sichote-Alin.

Zabytoe ore deposit is connected with the stock of Li-F granites which cut valanginian sandstones and sheets (130 Ma). These rocks were transformed into biotite metasomatites within 600 m from the contact (Popov et al., 1992). Ore bodies are represented by submeridional quartz-veins with wolframite, fluorite, topaz, cassiterite, beryl and micas.

Sm-Nd age of the ore veins 68±2 Ma is determined by isochrone method on wolframites and fluorites. Rb-Sr age determined on fluorite and orthoclase from one sample is 66 Ma. 4 samples of orthoclase form the errochrone with the age of 67±14 Ma. Rb-Sr age of metasomatites (70±1 Ma) coincides in the limits of analytical error with the age of vein formation and indicates that these processes were separated in time from crystallization of granites 95±15 Ma ago (Sm-Nd) (Belyatsky et al., 1994). The initial Nd isotope composition of fluorites and wolframites (ε=-1.3 ±0.5) is close to those of granites (ε=-0.7±0.5) and differs sharply from the Nd composition of biotite metasomatites (-7.7±0.5) (Fig. 1). Positive values of ε in orthoclases (+0.3 - +2.3) suggest the presence of mantle component in fluid composition at the earlier stages of vein formation. Rb-Sr isotope system of granites was disturbed by latter overprinted processes about 60 m.y. ago. The values of the primary Sr isotope composition in veins (0.712-0.713) and in metasomatites (0.717) are typical for crust material. According to Nd isotope composition it is possible to suppose that fluid of mantle origin was contaminated by the substance of granites and metasedimentary rocks and in the course of cooling off was acquiring more crustal characteristics. The

ore material was remobilized from the granites mainly. The spatial coincidence of ore veins with granite stock are explained first of all by the more weak tectonic zone of the stock in comparison with the host rocks and this why more favorable for ore fluid penetration.

The process of ore formation at Rudnoe ore deposit was quite different from the one discussed before. The vein field of ore deposit is composed by dislocated biotite metasomatites formed upon sandstones and aleurolites K_1 and T_3 (Vinogradova, 1984). Ore bodies represented by quartz-veins were formed in two stages: feldspar-wolframite-scheelitic and sulfide-carbonatic. Rb-Sr age of regional metasomatism is 87±10 Ma and the age of the first stage of vein mineralisation is 80±1 Ma (Krymsky et al., 1995). Sm-Nd isotope data do not permit to get the age calculations because of considerable variation of the initial Nd isotope composition in rocks and minerals. Sm-Nd isochron age of the wolframites is 78±32 Ma.

Sedimentary host rocks are characterized by considerable variations of Nd isotope composition: ε^{80} of sandstone -18, aleurolites -3.3 what is caused by the change of shares of Proterozoic crust material and young volcanics in sediment formation. Initial Sr isotope ratios of aleurolites - 0.714 and sandstones - 0.717-0.719 reflect the crust origin of their sources.

Biotite metasomatites have even more varying ε^{80}(from +2.9 till -15) and I_{Sr} (0.708-0.714) caused by heterogeneity of Nd and Sr isotope compositions of sedimentary rocks as well as by different range of reworking and assimilation of these rocks by mantle fluid.

Among vein minerals of the first high-temperature stage there is a trend to decreasing of ε^{80} from the more earliest minerals towards the more latest from +2.7 to -5.9 for orthoclase, from -3.3 to -10.0 for wolframites and from -4.2 to -11.9 for biotites and scheelites. This regularity can be caused by gradual increasing of crustal component share (or host rock) within the fluid. The initial Sr isotope composition of minerals of the first stage corresponds to 0.714. Minerals of the second low-temperature stage (fluorite and calcite) are characterized by ε^{80} from -6.2 to -11.5 and I_{sr}=0.716 which indicate the increasing role of crustal material in isotope balance of fluid (Fig. 2).

The obtained data prove that the source of primary ore fluid at Rudnoe ore deposit was the fluid separated from depleted mantle which later during its upraising assimilated sedimentary rocks. In the process of vein formation accompanied by temperature decrease the share of crustal material was increasing.

Thus, isotope investigations of these two ore deposits show that formation of wolframite ore deposit in this region is connected with the activity of contaminated mantle-crustal fluids. At the same time there can be spatial connection of ore veins with granites (Zabytoe ore deposit) without connection in time, but there can be no any relation with granites at all (Rudnoe ore deposit) and this allow to suppose the leading role of mantle fluids in the process of wolframite ore formation.

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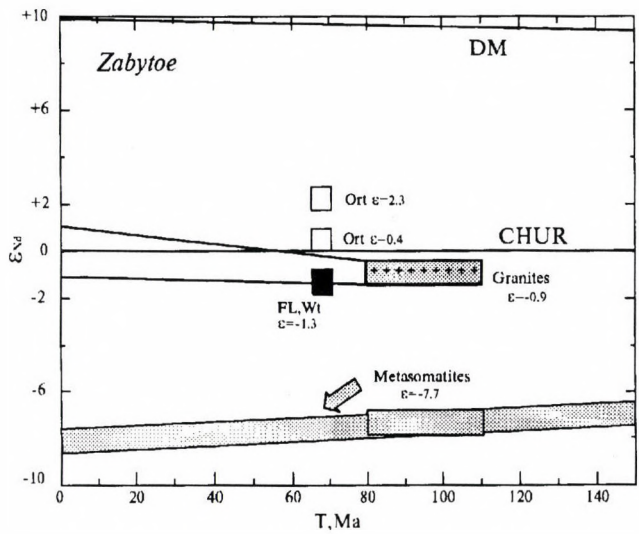

Fig. 1. Diagram ε_{Nd} vs. T (Ma) for host rocks and vein minerals of Zabytoe ore deposit. Fl, Wt and Ort - fluorites, wolframites and orthoclases, respectively.

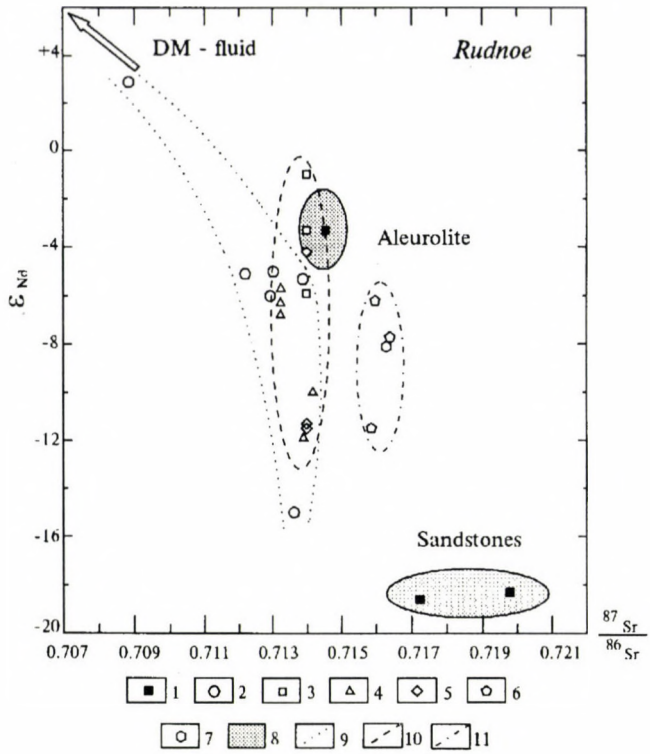

Fig. 2. Diagram $^{87}Sr/^{86}Sr$ vs. ε_{Nd} for host rocks and gangue minerals from Rudnoe ore deposit for time 80 m.y. ago.
The symbols are: 1-sedimentary rocks, 2- regional metasomatites, 3-7- gang minerals: 3- orthoclases, 4- scheelites, 5- biotites, 6- calcites, 7- fluorites. Fields: 8- sedimentary rocks, 9- metasomatites, 10- high-temperature veins, 11- low-temperature veins.

Determination of oxygen isotope fractionation between water and phosphate from living lingulides: potential application to palaeoenvironmental studies

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Lingulides are inarticulate brachiopods, with phosphatic shells, which live exclusively in marine waters. Their distribution is generally restricted to the continental shelf, within the 40° belt from temperate to equatorial areas. They show a range of morphological, physiological, and behavioural features that have remained remarkably constant since the Cambrian. The oxygen isotope fractionation between water and phosphate from living lingulides was determined as a tool to investigate the temperature and/or salinity of past coastal seawater. Oxygen isotope measurements were performed according to the silver phosphate method on a collection of lingulides coming from well-known and varied marine environments. *Lingula anatina* records the highest $\delta^{18}O$ values (22.8 to 23.1‰) for the relative cold waters (T°C = 12) of Japan whereas the same species gives $\delta^{18}O$ values in the range 21.6 to 21.9‰ for the tropical waters of New Caledonia. Similar $\delta^{18}O$ values (21.4 and 21.5‰) are provided by *Glottidia pyramidata* from Florida. *Lingula reevei* from Hawaii has a $\delta^{18}O$ value of 20.9‰ whereas the lowest $\delta^{18}O$ values (19.5 and 19.6‰) were found for the *Glottidia audebarti* specimens which live in the very warm waters (T°C = 28±1) of the Pacific coast of Costa Rica.

A global $\delta^{18}O$ variation of 3.5‰ was found for these lingulides which proves their good sensitivity to environmental factors namely the oxygen isotope composition and the temperature of seawater. Oceanographic data provided average temperature and salinity values in the living sites of the studied specimens. Least squares treatment of the data gave the following fractionation equation:

$$T°C = 112.2\pm15.3 - 4.20\pm0.71[\delta^{18}O(PO4) - \delta^{18}O(H_2O)]$$

which is similar to the equations determined by Longinelli and Nuti (1973a) and Kolodny et al. (1983) for other phosphate-bearing invertebrates and fishes. All these results suggest that a unique equation describes the phosphate-water fractionation of many marine organisms except for mammals. The absence of detectable isotopic fractionations which are produced by the so-called "vital effects" is a remarkable feature of the phosphate-water system which strongly contrasts with the carbonate-water system for which isotopic disequilibrium between the oxygen isotope composition of seawater and the shell carbonate is a common feature of many marine invertebrate species. The main result is the safe potential application of this isotopic scale to extinct species, opening thus the possibility of palaeoenvironmental investigations.

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Carbon stable isotope compositions of palynomorphs: an aspect of biodiversity through the Paleozoic

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The amplitude of stable carbon isotope fractionation was studied between various extinct palynomorph groups preserved together into sediments of Silurian to Devonian age. Variations in the $\delta^{13}C$ values related to distinct biological groups as well as their marine or terrestrial origin are examined to investigate more accurately the significance of the global $\delta^{13}C$ record of marine sediments through time.

Some of the analysed taxa clearly belong to the animal kingdom: graptolite sicula and rhabdosome fragments, scolecodonts, and eurypterid cuticles. Others correspond to marine paleophytoplankton usually regarded as green algae: leiospheres and *Marhanites* sp. Some organic walled microfossils are of unknown biological affinities i.e., chitinozoans and hydrozoans. Land derived palynomorphs include plant cuticles, tubular organic structures, and tracheids. The sampled localities belong exclusively to Gondwana and to Baltica paleoplates.

Most of the organic debris are of marine origin and their $\delta^{13}C$ values range from -30 to -26‰ for the Silurian and Devonian periods. These $\delta^{13}C$ values are in the same range than those reported for pre-Tertiary marine sediments and about several per mil lower than those measured in Holocene sediments. Low $\delta^{13}C$ values for old sediments may be compared to the plankton values found at high latitudes where cold waters can dissolve more

CO_2 than at low latitudes. A high pCO_2 in the Earth's atmosphere before Tertiary times was thus proposed as an explanation for the low $\delta^{13}C$ values of marine plankton.

Global $\delta^{13}C$ variations through time as records of paleoenvironmental fluctuations are delicate to assess for the following reasons 1) the organic fraction in sediments results from the accumulation of different plankton taxa whose specific metabolic pathways are unknown, 2) proportions and isotope compositions of terrestrial and marine organic reservoirs that contribute to the global $\delta^{13}C$ of the sediment are generally unknown.

In our samples, carbon isotope variations of 1 or 2‰ were commonly found, but not systematically, within various marine plankton taxa. Taxa-related $\delta^{13}C$ variations within a single sample seem to be a primary feature partly related to specific metabolic pathways. These internal $\delta^{13}C$ variations in a sediment may reach 4‰ when organic matter of terrestrial origin is present ($\delta^{13}C$ from -25 to -23‰). The amplitude of $\delta^{13}C$ variations in fossil organic matter generally does not exceed a few per mil δ at important stratigraphic boundaries thus confirming that the interpretation of global $\delta^{13}C$ variations through time must be very careful. We interpret the global $\delta^{13}C$ of organic matter in marine sediments as average values which integrate, in addition of chemical characteristics of surface waters (e.g. $[CO_2]_{aq}$), source- and species-dependent isotopic compositions. We consider that these $\delta^{13}C$ heterogeneities at the scale of a sediment sample could result from two main fluxes of organic matter organized in a bi-dimensional frame 1) the water column and 2) the oceanic currents and rivers.

We propose to examine $\delta^{13}C$ variations in the organic matter of marine sediments by using a selected palynomorph to avoid source and species-dependent isotopic signals. Such a protocole may serve to establish more reliable relationships between the $\delta^{13}C$ of organic matter and the chemical variables of the marine environment.

Nitrogen Stable Isotope Fractionation During Mineralisation of Sedimentary Organic Matter

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Key words: recent sediment, sedimentary organic matter, mineralisation, stable isotopes, nitrogen

Introduction

Particulate organic matter is partially decomposed in the water column, however, most of it is sedimented and represents an important source of nutrients for the water column. In general, the mineralisation of organic compounds can be considered as a set of redox reactions, most of them generated by aerobic or anaerobic micro-organisms. An isotopic fractionation of the main biogenic substrates such as CO_2, HCO_3^-, SO_4^{2-} or NH_3 occurs first as a consequence of inorganic reactions at exactly defined sites in the ecosystem (i.e. equilibration with the atmosphere, evaporation etc.). Further fractionation takes place accompanying biochemical reactions, where the isotopic selectivity of organisms depends mostly on availability of the substrate (Wada et al., 1993).

Nitrogen is a very important nutrient and its biogeochemical cycle is of great importance for the stability and relations in aquatic ecosystems. Its main phases are nitrogen fixation, mineralisation of organic detritus and release of NH_3, nitrification of NH_4^+, denitrification and fermentation of nitrate (Kinzig & Socolow, 1994). At each step nitrogen isotope fractionation occurs based on biological kinetic effects, where preferential uptake of ^{14}N by plankton results in reaction products that are depleted with ^{15}N and the residual fraction becomes gradually heavier.

We report the results of an on-going study of nitrogen isotope fractionation related to decomposition of organic matter in the lacustrine sediment of a eutrophic freshwater lake (Lake Bled, NW Slovenia).

Methods

The sampling and sample preparation is described in another paper (Lojen et al., this volume). Two sampling points were chosen - one in the deepest part of the lake (Western basin), where anoxic conditions prevail during the whole year except in two short periods of spring and fall overturn - and one in the shallow bay (Zaka) where the water is always oxygenated down to the bottom. In the pore water, NO_2^-, NO_3^- and NH_4^+ concentrations were determined. An HCNS elemental analyser was used to determine the total and organic carbon, nitrogen, phosphorus and sulphur concentration in the sediment. Stable isotope composition of dissolved nitrogen was determined on oven-dried samples containing 100 μg of nitrogen using a Europa 20-20 Stable Isotope Analyser with Anca SL preparation module. In the NH_4^+-rich samples, ammonia was fixed with sulphuric acid. $\delta^{15}N$ of the sediment was determined on bulk samples using the same equipment. The results are expressed relative to air in permil (‰).

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Results and discussion

In the pore water, total dissolved nitrogen (nitrate + nitrite + ammonia) is low down to the depth of about 10 cm below the water/sediment interface, but then it rapidly rises to reach up to 1800 μM in the anoxic part of the lake and about 1200 μM in the oxygenated bay. Nitrate is important only in the first two cm (up to 100 μM) of the sediment, then its concentration falls to values below 10 μM. We cannot rule out that this small amount is due to oxidation of ammonia because of improper sample handling. Such distribution of nitrogen - species is expected because of the low redox potential within the sediment. In the sediment, the fraction of organic nitrogen falls with depth from about 0.45 wt.% in the uppermost segment down to 0.10% below 25 cm. Also the organic carbon decreases from 4.5 to <2 wt.%, whereas sulphur increases slightly with the depth.

The isotopic composition of organic nitrogen in the sediment is shown in Fig. 1. In the oxygenated part of the lake (Zaka), where the influence of natural effluents of the lake is significant, it is independent of the depth and has $\delta^{15}N$ values around 6‰ in the surface layer of the sediment. No seasonal variation could be found. In the deepest part of the basin, $\delta^{15}N$ is lower in the first 10 cm of the sediment and then suddenly increases by more than 1 permil. Here seasonal dependence of N - isotopic composition was observed. In the spring soon after overturn of the lake, $\delta^{15}N$ of the surface sediment is higher than in the spring and summer. This shift can be attributed either to change in the organic matter itself (change in predominant biotic species related to temperature conditions, Schefer et al., 1995) or to a different mineralisation pathway in a more reductive environment which develops deeper in the sediment. Considering the difference in oxygen concentration between Zaka and the western basin, one can expect different planktonic populations which can differ in their trophic level and hence in their nitrogen isotopic composition (Wada et al., 1991). At the same time, the decomposition pathway of organic matter is different (and faster) in the oxygenated environment than in the western basin, where the hypolimnion is anoxic through most of the year (concentration of O_2 is lower than 0.1mg/l). Therefore we assume that differences in profiles of $\delta^{15}N$ vs. depth derive from changes in source organic material and from differences in pathways and rate of decomposition.

Isotopic composition of dissolved nitrogen in the pore water is not related to the depth nor to its concentration, however, it is in a perfect linear relationship to the isotopic composition of sedimentary organic nitrogen with $r^2>0.96$ (Fig. 2). Here a distinctive difference between two environments can be observed: in the upper 10 centimetres the correlation is obviously different than in the lower part of the sediment. Regularly, $\delta^{15}N$ values are up to 5‰ higher in the lower segment. Unexpectedly, observed $\delta^{15}N$ values for dissolved nitrogen were in some cases higher then those for sedimentary nitrogen. This clearly shows that more than one process is involved in the decomposition of organic matter and that the isotopic composition of dissolved nitrogen is changed in a secondary reaction. In the pore waters, many nanobacterial populations can be present with a considerable fraction of organisms that were smaller than 0.4μm and thus were not removed during filtration of the sediment and are known to be isotopically heavier than average populations (Altabet, 1990). So the positive shift in $\delta^{15}N$ can be attributed to the presence of bacterial colonies and related assimilation of ammonia (Hoch et al., 1992). The different correlation between $\delta^{15}N$ of dissolved and sedimentary nitrogen

in the upper and lower segments of the sediment is then attributed to the changes in redox potential and to the presence of microorganisms with different assimilatory capacities or their different abundance.

Conclusion

Stable isotope composition of nitrogen can be used to follow the extent and pathway of decomposition of sedimentary organic material. In oxygenated environments the mineralisation proceeds faster and particulate organic matter is partially decomposed to refractory substances (considering nitrogen!) before it settles at the bottom. In anoxic water, the decomposition is slower and is more intensive within the sediment, too. Dissolved nitrogen in the pore water is subject to secondary assimilatory reaction and thus to further isotopic fractionation which depends on the abundance and kind of predominant bacterial population.

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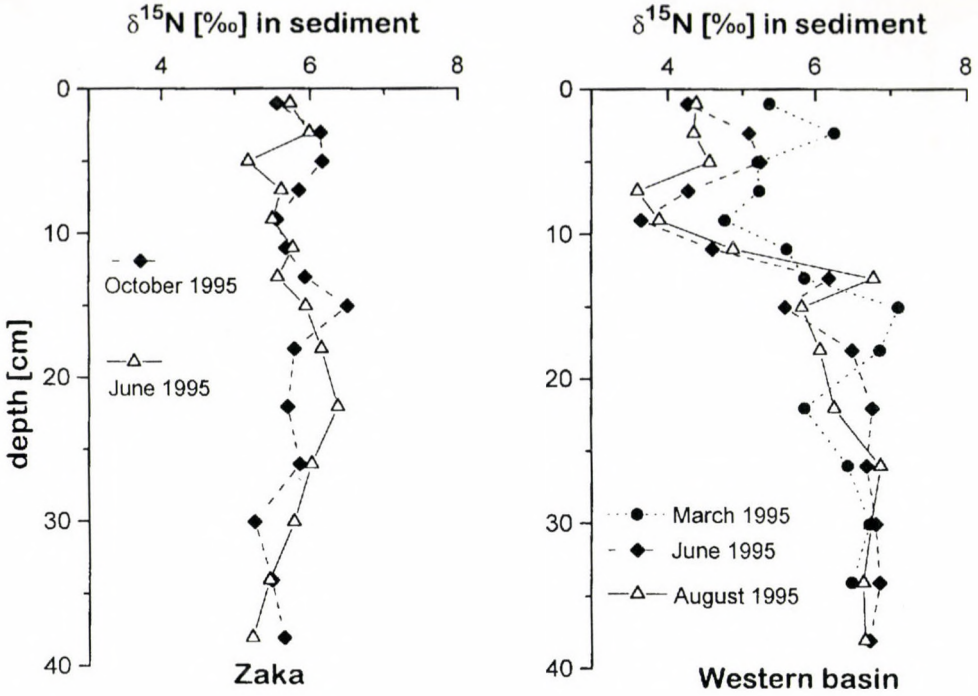

Figure 1: Relationship between $\delta^{15}N$ of sedimentary organic nitrogen vs. depth; in Zaka the water column is oxygenated down to the bottom whereas in western basin, hypolimnion is anoxic through most of the year.

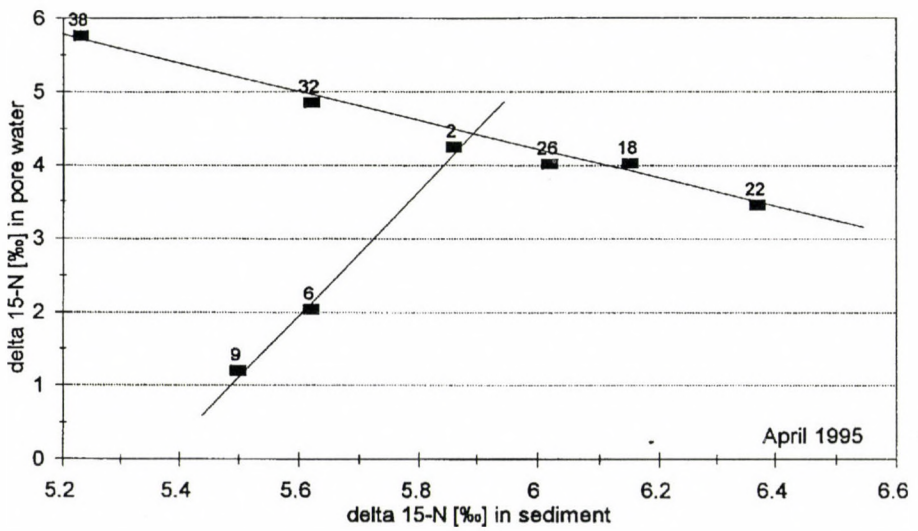

Figure 2: Relationship between $\delta^{15}N$ of dissolved nitrogen and sedimentary organic matter in Zaka in spring conditions.

A Stable Isotope Study of Recent Lacustrine Sediments (Lake Bled, Slovenia)

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Keywords: lake, recent sediment, stable isotopes, carbon, nitrogen, sulphur, methane

Introduction

Lake Bled is a postglacial subalpine lake located in the Eastern Julian Alps in the Radovljica basin, filled with fluvioglacial deposits. The hinterland of the lake is geologicllay composed mostly of Middle-Permian and Mesozoic carbonates. The lake is dimictic and highly eutrophic, with mean natural retention time of about 4.5 years (Leibundgut & Zupan, 1992). However, the ecological situation has been improving since intensive restoration measures were undertaken. These include a pipe line which introduces fresh water into the lake was installed and pumps out anoxic hypolimnical water. About one third of lake's total volume is thus exchanged yearly.

Due to supersaturation with nutrients, big planktonic populations develop. They are the main source of organic detritus, which partially decomposes in the water, while most of it is sedimented. So the sediment is the most important source of nutrients at least for the lower part of the water column, since fluxes of carbon, nitrogen and sulphur from the sediment upwards are all positive. In the deeper part of the lake, the whole hypolimnion is anoxic whereas in some shallower bays the water column is supersaturated with oxygen down to the bottom.

A stable isotope study of carbon, nitrogen and sulphur was used to follow the decomposition of organic matter at and below the sediment/water interface, with special emphasis on methane formation and on estimating the equilibria of the carbonate system in the pore water.

Methods

Separate studies of water column, sediment and pore water were performed. Samples were taken using a gravitational corer with Plexiglas tubes (35 mm I.D.) in the spring (March/April), summer (July/August) and in autumn (November) in 1983-89 and 1994-95. In the first period of sampling the sediment samples were cut, centrifuged at 8000 rpm and finally filtered. Recently the sediment cores were cut into 2 to 4 cm sections in a glove box in an inert atmosphere. Pore water was squeezed from the sample under 0.4 MPa N_2 through a 0.45μm membrane filter. Anion analyses (NO_3^-, NO_2^-, NH_3, H_2S, SO_4^{2-}, PO_4^{3-}) were performed using standard spectrophotometric methods. Metal concentrations were determined by flame - AAS (Ca, Mg, Na, K, Fe, Cr, Mn, Pb, Al), and P and Si by ICP-AAS. Total alkalinity was estimated as acid neutralisation capacity with 0,01 M HCl down to pH = 4,5 and the concentration of total dissolved inorganic carbon was calculated from total alkalinity

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and pH after Millero (1995) where factors describing salinity were neglected. Dissolved organic carbon was measured by IR spectrometry after high-temperature catalytic oxidation on Al_2O_3/Pt at 680°C. Isotopic compositions of carbon, oxygen, nitrogen and sulphur were estimated by mass spectrometry and expressed as relative (δ) values compared to international standards (PDB for carbon, SMOW for oxygen, air for nitrogen and CDT for sulphur).

In the sediment, $\delta^{13}C$ and $\delta^{18}O$ of carbonate were determined, as well as $\delta^{13}C$ and $\delta^{15}N$ of the organic fraction. Sulphur concentration in the sediment was too low to make an on-line isotopic analysis, so the sediment was annealed in O_2 to extract the organic and sulphide S - fraction, which was measured separately from the remaining sulphate. Mineralogical composition was determined using X-ray diffraction. Scanning electron microscopy with energy dispersion spectrometry (SEM/EDS) was used to study the morphology and composition of single grains.

Results and discussion

The sediment is mostly an organic-rich clayey silt with 5 - 80% carbonates and an organic carbon content of 1.8 to over 4.5% wt. The concentration of organic nitrogen was measured to be between 0.1 and 0.4 wt.% and total sulphur between 0,08 and 0,3%. The mean C:N ratio is 11.8 and N:P around 22. This means that the stoichiometry of the organic phase is quite different from the Redfield's one (C : N : P = 106 : 16 : 1), but still in the range reported for freshwater lakes (Hecky et al., 1993).

Phase analysis of the sediment showed that low-Mg calcite prevails. Although some dolomite is also present, it is mostly detritic. Among non-carbonate phases quartz and mixed-layer clay minerals are most abundant. As already reported in literature, some autigenic pyrite was found in the deepest part of the lake (Molnar et al., 1978).

A previous study of more than 100 sediment samples (Dolenec et al., 1994) showed that in some places a significant amount of detritic carbonate is present and that the carbonate phase of the sediment can be divided according to its C and O isotopic composition into four groups: (1) sediment of stagnant anoxic environment, (2) lacustrine chalk (present in the shallow plateau in the SW part of the lake), precipitated in open-basin conditions, (3) sediments with considerable amount of detritic phase and (4) sediment formed below the interface with autigenic calcite modified by postdepositional changes and influenced by ^{13}C depleted methane and ^{13}C enriched organic matter from the lake bottom. Observed $\delta^{18}O$ - $\delta^{13}C$ covariant trends indicate that precipitation of autigenic calcite must take place in the sediment. Based on isotopic data we tried to estimate under which conditions the precipitation is possible and which is the most important source of carbon to form autigenic carbonate phases.

Calculation of saturation indices of calcite, aragonite and dolomite in pore waters showed that they can either dissolve or precipitate, depending on the actual physicochemical conditions. During the colder period of the year, precipitation is more likely since saturation indices are positive for all three minerals, whereas in the summer dissolution is indicated. However, saturation states differ in different parts of the lake. The correlation between $\delta^{13}C$ of carbonate and sedimentary organic matter clearly indicates that decomposing organic matter can be a source of carbon for the precipitation of carbonate solid phases. The SEM analysis of the sediment 5 cm below the sediment/water interface clearly showed dissolution forms of calcite grains

and some cryptocrystalline aggregates of carbonate minerals which can be described as autigenic formations, where Ca and Mg are represented in different ratios, although Mg is regularly much lower than Ca.

$\delta^{13}C$ of sedimentary organic carbon (SOC) shows values between -27 and -38‰ PDB. This is much lower than the $\delta^{13}C$ of most common plankton species (-15 to -26‰), water plants (-11 to -26‰) or leaves and pollen of the nearby trees (-26 to -30‰). Therefore we assume that adsorbed hydrocarbons and nanobacterial populations (which are widely abundant in the sediment) are lowering the average δ^{13} of total SOC (Freeman et al., 1990). At some sampling points $\delta^{13}C$ vs. depth follows a Rayleigh-type function, however, such a relation is rather exceptional. As expected and reported in literature (Bauer et al., 1995), $\delta^{13}C$ of dissolved organic carbon (DOC) shows similar values to SOC, however, the range of values is not so broad (between -26 and -29‰).

Isotopic composition of dissolved inorganic carbon was found to be linearly dependent on its concentration. However, most interesting are the profiles of $\delta^{13}C$ of DIC vs. depth. A strong increase - in some cases of up to 30‰ - can be observed in the first 40 cm of the sediment. $\delta^{13}C$-DIC in the supernatant and in the first 2 - 5 cm are very similar (between -15 and -8‰, depending on O_2 concentration in the supernatant and the season), but then it slowly rises. A sudden increase to positive value follows in the depth of about 10 - 15 cm in samples taken from the oxic part of the lake or even in the first few centimetres of the sediment column in the anoxic part of the lake. Here, values of up to +16‰ were measured. Since $\delta^{13}C$ of autigenic carbonates are between -4 and -2‰ and those of the detritic phase up to +4‰, formation of methane can be the only explanation for such behaviour of $\delta^{13}C$. In fact, methane was found to be present in the sediment. Measurements of its $\delta^{13}C$ showed values around -50‰, which is quite high. However, this not necessarily the isotopic signal of as-formed methane; its carbon may be significantly more depleted with ^{13}C since the presence of up to 1mM sulphate in the pore water down to 50 cm below the sediment/water interface indicates that oxidation of methane can take place. This can be an explanation, too, for relatively low $\delta^{13}C$-DIC values in the upper segment of the sediment and in the supernatant. Although sulphate reduction and methane formation are reported to be competitive processes (Alperin et al., 1992, Blair et al., 1994), our results agree with Oremland et al. (1982, 1987) that methane can form within the sulphate-rich zone.

Isotopic analysis of dissolved sulphate in the supernatant showed values of $\delta^{34}S$ of about 9‰, which correspond to those of sulphate from the surrounding rocks. This means that dissolution of detritic material is still the main source of dissolved sulphur. Very similar $\delta^{34}S$ values were found in the sedimented sulphate, too. Sedimentary organic sulphur has $\delta^{34}S$ of about 4‰, a value that corresponds to those reported by Peterson and Howarth (1987). Since the assimilation of sulphur by micro-organisms causes a rather small isotope fractionation, the lower value than that of sulphate is explained by sulphate reduction, which indeed takes place in the examined pore water.

Isotopic studies of sedimentary nitrogen showed that $\delta^{15}N$ has no regular relation to the depth or N - concentration in the sediment or in the pore water. As with organic carbon, in the case of nitrogen no Rayleigh-type decomposition could be observed in any case. $\delta^{15}N$ of sedimentary organic nitrogen varies between 4 and 8‰ and those of dissolved nitrogen between +1 and +8‰. At all the sampling points and in any season, there exists a strictly linear dependence between $\delta^{15}N$ of the

sediment and dissolved nitrogen in the same depth segment. A second paper deals with nitrogen isotope fractionation in the sediment in more detail.

Conclusion

Isotopic study of C, O, N and S was used to follow the decomposition of organic matter and to define the carbonate equilibrium in the pore water system of Lake Bled. Particulate organic matter was found to be the main source of carbon for the precipitation of autigenic carbonate phases, which seasonally can take place dependent on pH, temperature and redox conditions at the lake's bottom and within the sediment. Isotopic composition of carbon in DIC clearly shows that formation of methane takes place within the sulphate-rich zone. This indicates that in observed system methanogenesis and sulphate reduction are not competitive processes.

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ISOTOPE-GEOCHEMICAL CHARACTERISTIC OF GROUNDWATER IN THE SOUTH LITHUANIA

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Keywords: tritium, radiocarbon, helium, stable isotope, residence time.

The task to estimate processes of groundwater forming in the South Lithuania in detail has appeared because of diversity of natural conditions and technological purposes of society. From the geomorphological standpoint, this district is sandy plain, where inhabitants of small towns use groundwater occurring in alluvial deposits at depths of 15-20 m. From the geostructural standpoint, this district is located on the slope of Byelorussian-Mosurian anteclise, where crystalline basement occurres not deep (350 m). In addition, here the iron ore is found and in due course of time it could be exploited. On the other hand, this district has undergone though small but perceptible influence of the Chernobyl NPP accident (here and there the fallouts of cesium-137 are up to 10 kBq/m^2, when before the Chernobyl NPP accident the global level of cesium-137 has been in the Lithuania about 2 kBq/m^2.)

From the hydrodynamic standpoint, three different objects have been selected for isotope-geochemical investigation in detail (Fig.1).The first of them, it is a groundwater from basin of closed undrained lake. In this district in such condition often waterwork are established. The second, it is a groundwater from environs of the Margiai bog (a low-land bog).This bog (on area 139 ha) is located in sandy deposits of drained zone with season recharge in the valley of small rivulet. Higher contamination by cesium-137 is characteristic, namely, to this territory. The third object, is the system of groundwater from the Varėna ore-bearing joint, which includes a number of aquifers from Quaternary to Proterozoic basement by their age.

The data of tritium, radiocarbon, carbon-13, deuterium, oxygen-18, elemental helium and chemical composition have been used in investigations. The measurements of isotopes have been carried out according to the standard scale: for tritium - using an electrolytic enrichment and scintillation radiometry, for radiocarbon - benzene form and scintillation radiometry, for elemental helium detector of quartzeous glass membrane, for stable isotopes - mass spectrometry. The most significant data of investigations are presented in the Tables I, II. For interpretation of investigations data the most of ordinary procedures: evaluation of parameters of water exchange time according to H-3 data, determination of radiocarbon age correcting it according to C-13, compilation of diagrams "radiocarbon age - changes of stable isotopes", etc., have been used. The water residence time has been evaluated according to exponential model [Maloszewski and Zuber, 1982]. Correction of radiocarbon age according to C-13 has been carried out as it is given [Fernonsky et al., 1984]. On basis of these procedures, the parameters of water exchange intensity, peculiarities and time of groundwater forming of investigated objects are evaluated. Virtually, these objects illustrate typical cases of groundwater forming in the district under investigation [Juodkazis et al., 1995].

The conceptual hydrodynamic model of the Lake Glebas environs is represented in the Fig.2. According to tritium data and distribution of water residence time, it is possible to state

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that the water of lake does not drain the ground horizon, but extends it and makes a certain hydrogeological window: the groundwater residence time decreases under the bottom of lake.

Another distribution of tritium, water residence time and radiocarbon is observed in the environs of bog, which drains the upper part of shallow groundwater horizon, and the water from the lower part of horizon is unable to penetrate through the low permeable layer (Fig.3). Here the water exchange gets slower, the tritium concentration is close to zero and the radiocarbon age is about 4000 years. According to isotope data, the "inactive" water is found under the bottom of bog. It is characterised by higher salinity (600 mg/l) than in peripherial parts of the bog (200 mg/l) and by high NH_4^+ concentration (up to 70 mg/l). These two examples characterise peculiarities of water exchange in the uppermost part of hydrosphere.

In the Varėna ore-bearing joint the peculiarities of isotope composition of groundwater are studied in vertical direction - Quaternary intermorainic horizon, Lower Cretaceous horizon, Upper Permian horizon, Cambrian-Vendian horizon (Fig.4). In the first two horizons the fresh water is found and deeper-water is mineralised: in the Permian horizon salinity is 2900 mg/l., in the Cambrian-Vendian 7700 mg/l and in the crystalline basement- 25900 mg/l. The traces of tritium (up to 0.3 TU) are fixed up to the Permian horizon, the water residence time is >1200 years (beyond the limits of method) in the whole section. Radiocarbon age changes from 3200 years in the Quaternary horizon to 8000-14000 years in below occurring horizons. The isotope-geochemical data indicate an active water exchange in the whole section. In the investigated plot (block of boreholes No 20171), which is the zone of discharge of deep horizons, also an influence of the post glacial factor could be observed, though the paleowater is almost changed because of active present exchange and near located zone of recharge. However in the diagram of "radiocarbon age - changes of oxygen-18" the tendency to "lightening" of isotopic composition is observed by the depth. The high water salinity, where the radiocarbon age is 10000-14000 years, could be related with cryogenic metamorphization of groundwater. The further exhaustive studies could confirm or deny the above mentioned resolution.

In the same territory, using isotope-geochemical methods, the important effects for protection of groundwater, as the effect of hydrogeological window in the zone of closed lake, the effect of "inactive" water in the zone of bog, foreknown forecasted post glacial effect in the zone of deep horizons are observed and evaluated.

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Table I. Tritium and stable isotope concentration in groundwater

Sampling place, borehole No, aquifer	Depth, m	Date	Tritium, TU	$\pm 1.5\sigma$	δ^2H, ‰	$\delta^{18}O$, ‰
Varėna district, Margiai environs						
1 (excavation)	0.8-0.9	1993.06.17	16.1	2.5		
680, Q	8-9	1993.06.17	24.6	3.3		-12
684, Q	8-9	1993.06.17	0	1.2	-81	-10.4
		1994.10.07	0.4	0.1		-10.0
686, Q	1-2	1993.06.17	25.2	3.4		-11.9
687, Q	5-6	1993.06.17	19.2	2.8		
682, Q	13-14	1993.06.17	0	1.2		-10.5
1678, Q	16.6-18.6	1993.06.17	0	1.2		
2 (excavation)	0.8-0.9	1994.10.07	12.7	1		
Water work No 1 of Varėna						
7, Q	25-30	1993.06.16	34.1	4.3		
Varėna district, station of Lake Glebas						
1371, Q	15-16	1994.10.06	9.5	0.7		
1369, Q	15-16	1993.06.16	7.3	1.6		
		1994.10.06	7.6	0.6		
1040, Q	7-8	1993.06.16	39.7	4.8		
		1994.10.06	27.6	2.1		
1376, Q	12-13	1993.06.15	18.1	2.7		
		1994.10.06	41	3		
1377, Q	12-13	1993.06.15	53.3	6.1		
		1994.10.06	10.1	0.8		
1378, Q	12-13	1994.10.06	14	1.1		
Varėna district, hydrogeological station						
20171, Q	70-75	1995.10.09	0.3	0.2		-10.5
20171, K_2	85-100	1995.10.09	0.6	0.2		-10.9
20171, K_1	178-187	1995.10.09	0.2	0.2		-10.9
20171, P_2	250-257	1995.10.09	0.3	0.2		-10.9
20179, P_2	242-260	1995.02.02	0.3	0.2	-81	-11.0
20171, ϵ_1-PR_2v	310-320	1995.10.10	0.1	0.1		-11.6

Table II. Radiocarbon age of groundwater

Sampling place, borehole No, aquifer	Depth, m	Date	^{14}C (DIC), pmC	^{13}C, ‰ PDB	^{14}C age, years	He, $x \cdot 10^{-4}$ %
Varėna district, Margiai environs						
684, Q	8-9	1994.10.07	23.6	-6.9	4100	
		1993.06.17		-6.6		
Varėna district, hydrogeological station						
20171, Q	70-75	1995.10.10	40.8	-10.7	3200	14
20171, K_1	178-187	1995.10.09	10.95	-11.2	14200	105
20171, P_2	250-257	1995.10.09	18.1	-11.0	9980	2250
20179, P_2	242-260	1995.02.02	10.4	-10.0	13700	
20171, ϵ_1-PR_2v	310-320	1995.10.10	7.9	-8.1	14200	2900
20173, PR_1	372-415	1994	22.6		8160	4500

Fig.1. Location of the investigated territory.

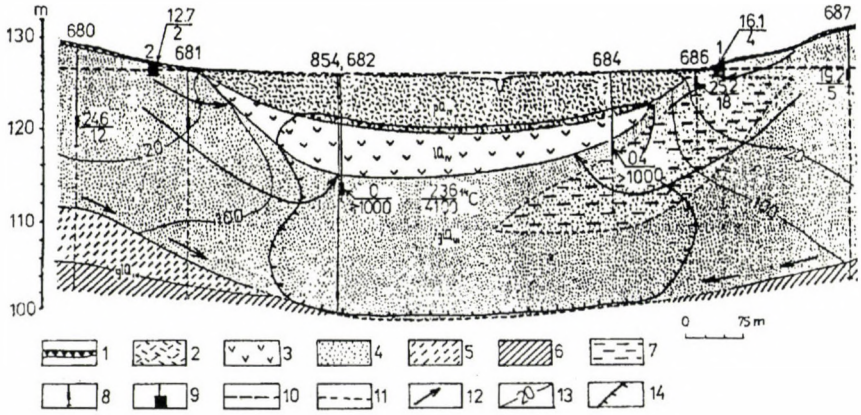

Fig.2. Distribution of the groundwater residence time in environs of bog along the hydrogeological profile: 1- soil, 2- peat, 3- sapropel, 4- sand, 5- sandy loam, 6- loam, 7- aleurite, 8- borehole under observation, next to it - the tritium concentration, TU - in numerator and residence time, years - in denominator (radiocarbon data: concentration, pmC- in numerator and radiocarbon age, years- in denominator), 9- excavation under observation, 10- level of groundwater, 11- level of surface water in the bog, 12- direction of water stream, 13- isoline of residence time, 14- zone of "inactive" water.

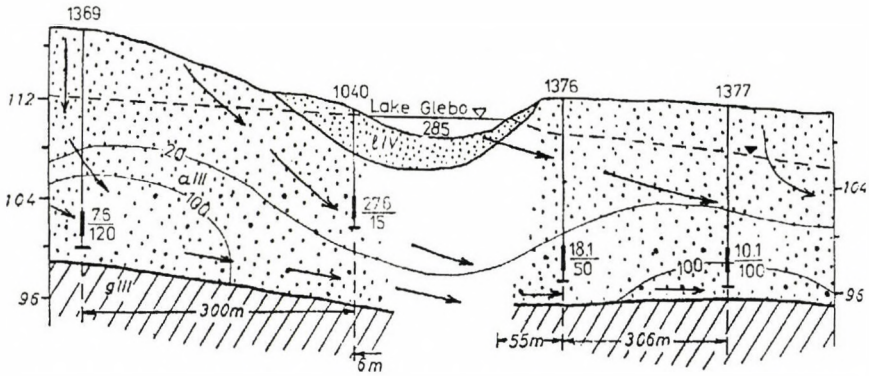

Fig.3. Distribution of groundwater residence time in the Lake Glebas environs (legend in Fig.2).

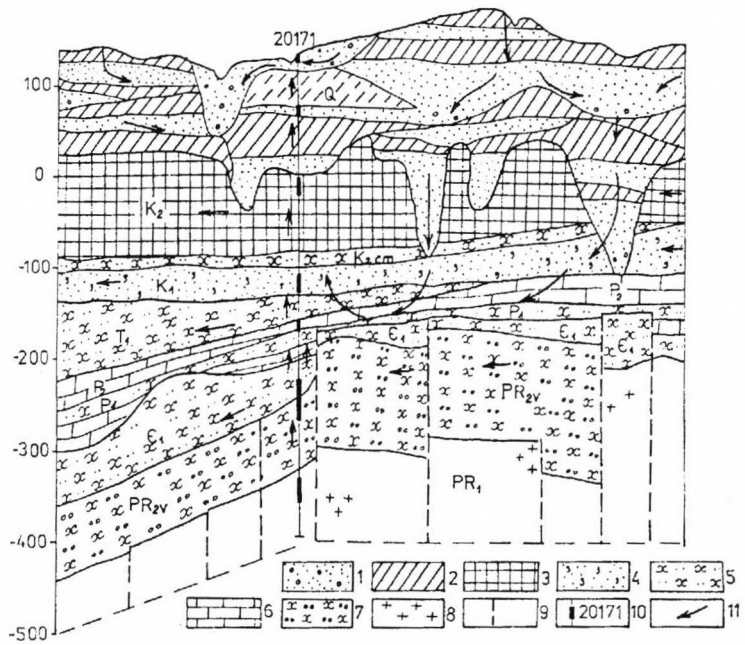

Fig.4. Hydrogeological scheme of the Varėna ore-bearing joint (according to manuscript data of the Lithuanian Geological Survey): 1- various sands, 2- loam, 3- chalk, 4- glauconitic sand, 5- sandstone, 6- limestone, 7- gritstone, 8- granite-gneiss, 9- tectonic faults, 10- borehole under observation, 11- direction of water stream.

IS A PART OF CRYSTALLINE CORE OF THE VEĽKA FATRA MTS. THRUSTED OVER MESOZOIC CARBONATE ROCKS? - RESULTS OF A STABLE ISOTOPE STUDY

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Keywords: carbonate, stable oxygen isotope, stable sulfur isotope,

Group of Slovak core mountains, to which Veľká Fatra Mts. belongs, is generally characterized by the presence of crystalline core, composed of metamorphic rocks and granitoids, and a system of Mesozoic nappes, overlying the core and its Mesozoic envelope and laying one on the another, thus forming several horizons of the Triassic limestone and dolomitic aquifers (Maheľ 1967, Maheľ 1978, Polák - Kohút 1990, Kohút et al 1992, Kohút et al. 1993). Groundwater flow in these mountainous conditions is controlled by the position of the intersections of carbonate rock outcrops with local or regional erosion base level.

Because of the importance of karstic groundwater sources in these aquifers, 30 springs and one brook which represented all major karst-fissure springs and hydrogeologic structures in each part of the mountain range were monitored to observe the oxygen (every sampling) and hydrogen (three times for every source) isotope composition of the spring waters, and stable isotopes of DIC (once) and sulphatic sulphur (once), chemical composition (three times) were analysed as well. The monitoring regime lasted from December 1991 to July 1993, the sampling frequency being roughly two months (a total of 9 series of samples were collected for each spring).

The average $\delta^{18}O$ contents from all analyses were then added into the altitude - $\delta^{18}O$ relationship. We thus resolved a parametric equation expressing the linear relationship between $\delta^{18}O$ and mean altitude of the recharge area. The values calculated by us for waters from single month $\delta^{18}O$ values of Veľká Fatra springs are varying from 0,103 to 0,148 ‰ per 100 m with 0,118 ‰ m for mean value per 100 m of altitude. Quality of lines is quite high, R2 factor vary from 0.66 to 0.99 with mean 0.89 (Malík et al. 1993, Malík et al. 1994, Michalko et al. 1993).This result is similar to data from northern Switzerland where Pearson Jr. et al. (1991) determined a change in the oxygen isotopic composition around 0.2 ‰ per 100 m and Holko (1995) who from southern slopes of Western Tatras presents adequate values as 0.1 to 0.2 ‰ per 100 m. Very similar results we received from altitude/temperature relationship. As the duration of the measurements was relatively long and its frequency short, and it is covering practically all year seasons, the calculated average isotopic composition of waters from individual sources could fairly reliably indicate the reality. Oxygen shift as a due of water - rock interaction could be neglected because all waters are cold (5 - 13 °C) excluding thermal water from Turčianske Teplice spa, and because of isotope hydrogen - oxygen relations (Mansell, 1994). Nevertheless, variations in oxygen isotopic composition in investigated springs suggest considerable stability of the otherwise variable values in karst structures probably due to extensive mixing of waters from large water-bearing regions. Moreover, their average composition corresponds to the average altitude of known springs and/or their recharge areas. This technique allowed us to rule out or confirm some potential recharge areas of certain groundwater sources (springs

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Jazierce, Hradská - Podhradie, Salatín 1 and 4, Malá and Veľké Cenovo, Rakytov) or indicated that some springs were recharged from surface streams (Lazce, Pri starej priehrade, Havranovo, Starý mlyn, Generál Čunderlík). The hydrologic time series analysis also showed important differences in their yield regime.

As most sulphur in groundwaters of the area concerned came from Werfenian ($\delta^{34}S \approx 25$ ‰) and Keuper ($\delta^{34}S \approx 14$ - 18 ‰) sediments, we decided to verify this fact by isotopic analyses of dissolved sulphatic sulphur. Kartesian diagrams were employed to indicate how sulphate content in spring water depends on sulphur isotopic composition. We expected a bimodal distribution with projection points clustered around two δ 34S values typical of the Keuper and Röt. However, the actual pattern shows particularly clearly that the curve is a mixed one, one member being sulphate-rich waters with heavy-isotope sulphur and the other sulphate-low waters with negative $\delta^{34}S$ values. A model involving the dissolution of gypsum and the associated incongruent dissolution of dolomite has been put forward, this has been supported by comparison with a chemical mass balance model (Mansell, 1994). Sulphates in the first group came from Lower - Middle Triassic marine evaporites, but the source of sulphur in the other member is unclear - the sulphur could have been derived from sulphides (but low contents and total hydrochemical character of water) or it can be of biogenic origin. We also assume that the three springs represent another mixing line of Keuper sulphates and sulphate-low waters with negative $\delta^{34}S$ values. Other springs, whose groundwaters circulate in carbonate masses without obvious sulphur occurrences, fall into a single point. Both sulphate contents and isotopic composition of their sulphate sulphur (SO_4 content is approx. 20 mg/l, $\delta^{34}S$ = approx. 5 - 7 ‰) do not exceed background values. The origin of this sulphur is difficult to explain. It could have come from minerals (pyrite) disseminated in rock, but such rock types contain very little sulphur. Another possible source of sulphur is precipitation. The average (10 year) sulphate content in winter precipitation fat Donovaly is 4.19 mg/l (Vrana et al. 1989). The isotopic composition of sulphur in precipitation ranges from values typical of modern marine sulphates to negative values due to human activities (industry). An analysis of sulphates dissolved in snow precipitation in Bratislava yielded results similar to those from the above springs. Further dissolution of sulphates from the traditional source rocks in the Western Carpathian Mesozoic (Permian, Lower Triassic shales, Carpathian Keuper shales) subsequently rises the soluble sulphate content reflecting the isotopic composition typical of the respective source rocks modified by mixing with the "background" isotopic composition which in accordance with the mixing rule also changes $\delta^{34}S$ values.

It became apparent, after the water mass balance analyses, that there are no, or very reduced infiltration possibilities for groundwaters of Matejková and Bukovina, Jazierce, Parohy and Biele vody springs at the eastern edge of the Veľká Fatra Mts. for such amounts of groundwaters (110 and 60 l/s respectively), in these climatic conditions with 400 - 500 mm of effective rainfall, about 10 km^2 of outcropping karstified carbonate rocks are "required". They can be found in the neighbouring hydrogeological structure isolated by crystalline core of the Ľubochniansky massive with remarkable higher altitude. This group of springs shows $\delta^{18}O$ values typical for recharge areas situated in higher altitudes then their apparent recharge areas as well. From this we concluded at least part of water from this springs is infiltrated "behind" the crystalline core which is supposed to be a part of crystalline mass, underlying all younger units and from hydrogeological point of view, isolating the karstic hydrogeological structures. There are two possible paths for water to pass the basement: highly fractured or opened fissures in crystalline core or suppose that Mesozoic aquifer is not disconnected under crystalline. After the chemical analyses it was discovered that waters appearing in springs do have quite high rate of T.D.S. ranging from

410 to 555 mg/l (and 1410 mg/l in the case of Matejková pod pňom spring), bicarbonates from 219 to 267 mg/l and sulphates 44 - 181 mg/l (781 mg/l in the case of Matejková pod pňom spring), and should be considered as they were not in contact only with crystalline (factor Sr/Ca*1000 is lower than 9,5 and Mg/Ca lower than 0,58).
Mansell (1994) argue that inorganic carbon is from Mesozoic rocks only and was not in contact with atmospheric CO_2. $^{87}Sr/^{86}Sr$ analyses are all higher than any Mesozoic sea water (0.708104 - 0.708283), but not enough to justify the proposition for involvement of basement in their chemistry (Veizer, personal communication).

Our results, concerning the use of isotope geology and hydrological methods in one hand, had pointed out the possibility of an "underground" connection of groundwaters between two karstic hydrogeological units, previously supposed to be isolated by crystalline core. The possible overthrusting of the crystalline masses as a part of Cretaceous nappes over the other Mesozoic rocks became therefore more evident.

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Petrographic and isotopic investigations of calcites from the Holy Cross Mts, Poland

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KEY WORDS: CARBON, OXYGEN, SULFUR, STRONTIUM ISOTOPES, CALCITES, HOLY CROSS MTS POLAND

This report presents the results of petrographic and isotopic (table 1) investigations performed on calcites from the Holy Cross Mts, central-south Poland (Fig.1). In general, 5 phases, i.e., A - Variscan (Visean/Nammurian), B - older Postvariscan (Late Carboniferous through Permian to the bottom of Zechstein conglomerates), C and D - younger Postvariscan (Permian/Triassic and middle/late Early Triassic), and E and F - Cimmerian-Alpine (Late Jurassic and Late Cretaceous), have been distinguished. This division has been confirmed by the highly diverse $\delta^{13}C$ i $\delta^{18}O$ values of these calcites clustered in 4 populations (Fig.2).

The Variscan calcites (phase A) are represented by 3 generations and occur primarily in the western part of the region. White calcite veins are as much as several centimeters thick; in places, they are associated with quartz crystals reaching 3 cm long, as well as with scattered Fe and Cu sulfides, barite, and organic matter (asphalt, ozokerite etc). These calcites are featured by prevalent positive $\delta^{13}C$ values; the latter correspond to those in hostrocks, i.e., in Middle and Upper Devonian limestones (from 0.31 to 3.23‰). The $^{87}Sr/^{86}Sr$ ratio indicates seawater as a hydrothermal conveyor (table 1).

The older Postvariscan calcites (phase B) are scarce and occur in the form of thin veins up to 2 cm in thickness, as well as pebbles embedded into Zechstein conglomerates. The number of generations is unknown due to the lack of dated deposits spanning the Upper Carboniferous to the bottom of the Zechstein. These calcites are white, in places pink. Compared to other calcites from the Holy Cross Mts, they are featured by the highest level of rare earth elements, especially Ce (36 ppm), Eu (2,3 ppm), Nd (36 ppm), Tb (1,3 ppm) i Yb (1,9 ppm). Some of the calcites contain Pb, Zn and Fe sulfides. Nearly all the $\delta^{13}C$ values are negative (table 1).

The "rose-like" calcites (phases C and D) are most common and include at least 10 generations (Migaszewski et al., 1994). The youngest generations contain dispersed Pb and/or Cu sulfides, and barite. These calcites occur within the same fault system. Nearly all these faults extend in the close to N-S direction cutting different consolidated Variscan structures. Calcite veins reach as much as 42 m thick. This unique structuro-tectonic position of the "rose-like" calcite indicates a rare geologic event that took place here in Early Triassic time. According to Migaszewski (in press), the Holy Cross Mts area probably shifted toward NW along the western margin of the East European Platform. This shift must have been coupled with a slight clockwise rotation. These two combined movements of the crystalline basement brought about forming echelon faults featured by a close to N-S strike. The produced heat was enough to warm up the seawater and to trigger its circulation. Nearly all these calcites reveal the negative $\delta^{13}C$ (table 1). The same $\delta^{13}C$ (-4.70 to 0.67‰) is observed in the

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calcitic-iron cement of Zechstein conglomerates (Migaszewski et al., 1995). The $^{87}Sr/^{86}Sr$ ratio (table 1) and the lead isotope composition in galena derived from the final generations of the "rose-like" calcites (Zartman et al., 1979) indicate no connection with the upper mantle source. In additon, no correlation between the $\delta^{13}C$ and the $\delta^{18}O$, as opposed to that in Permian/Triassic, Tertiary and Quaternary dripstones and flowstones of the Holy Cross Mts, and Quaternary "calcite groats" from the "Chelosiowa Jama" cave near Kielce (Migaszewski et al., 1994; Durakiewicz et al., 1995), has been noted.

The Cimmerian-Alpine calcites form thin white veins reaching several centimeters in thickness. Most of them (particularly within Turonian deposits) are accompanied by cherts. They have been traced in the southwestern margin of the Holy Cross Mts Paleozoic inlier. All the $\delta^{13}C$ values are positive (Table 1).

The calcites from the Holy Cross Mts formed under different geologic conditions: from a typical marine off-shore zone (phases E+F), through marine relict basins originated at the end of Variscan movements (phase A), to a terrestrial environment (phase B), at the final stage with strongly developed karstic processes (phases C+D). The marine provenance of the E and F phase calcites has been proved by the presence of fossil formation of sea-floor hot springs in Upper Cretaceous rocks (Migaszewski et al., 1987, 1995) and the $^{87}Sr/^{86}Sr$ ratio varying from 0.707269 ± 11 to 0.708129 ± 12. In turn, the continental origin of the C and D phase calcites has been evidenced by their strongly variable isotopic composition (C, O and Sr) and the presence of characteristic elongated inclusions. The development of karstification during precipitation of these calcites has been supported by a large number of different forms resembling flowstones and dripstones, as well as by karstic authigenic and allogenic intercalations, karstic-tectonic breccias etc.

The simultaneous determinations of the $\delta^{18}O$ and homogenization temperatures of gaseous-liquid inclusions in the same calcite crystals indicated that the hydrothermal fluids were primarily of marine provenance (Fig.3). This procedure was used previously for massive dolomites (Migaszewski, 1991). The mean $\delta^{18}O_{SMOW}$ is 1‰ being close to that found in mid-ocean hydrothermal fluids (±1‰); it is completely different from the $\delta^{18}O_{SMOW}$ for meteoric waters (-5 to -22‰).

No spatial variability in the isotopic composition of the examined calcites has been noted. Besides, samples collected from deep boreholes (for instance from 2,826.4 m in borehole Ostałów PIG 2 located about 50 km north of Kielce) do not reveal high negative $\delta^{18}O$ values (-4.13 to -2.73‰), i.e., high crystallization temperatures (42-35° C).

The results of petrographic and isotopic investigations performed on calcites differently highlight the problem of the age and the origin of ore mineralization in the Holy Cross Mts. Pb, Cu and Zn sulfides are connected mainly with phases D, in places B, C and A, whereas barites with D, sporadically A. The $\delta^{34}S$ in galena, which occurs in calcite veins, varies from -13.24‰ to 11.63‰, and in barites from 16.43‰ to 30.02 ‰. In turn, the $\delta^{18}O_{SMOW}$ of these barites ranges from 20.07‰ to 12.08‰. The latter values correspond to a temperature 52-124°C.

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Table 1 Isotope composition of principal phases of calcite mineralization in the Holy Cross Mts

Phases	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	T°C	$^{87}Sr/^{86}Sr$**
A (Variscan)	-1.73 to 2.27	-19.37 to -4.19	168-37	0.709325±9 to 0.709480±13
B (Older Postvariscan)	-2.32 to 0.23	-10.43 to -3.89	71-35	-
C+D (Younger Postvariscan)	-7.89 to 1.25	-14.11 to -0.91	122-25*	0.708689±9 to 0.711620±10
E+F (Cimmerian-Alpine)	1.28 to 2.67	-8.69 to -5.87	58-47	0.707269±11 to 0.708129±12

* The $\delta^{18}O_{SMOW}$ of the hydrothermal fluid = 1‰ was calculated on the basis of the $\delta^{18}O_{PDB}$ and homogenization temperature measurements of gaseous-liquid inclusions derived from the same calcite crystals (Fig.3)

** $^{87}Sr/^{86}Sr$ for contemporary seawater is ~0.709 being a mean value derived from mixing terrestrial (~0.711) and upper mantle waters (~0.703); a propotion 4:1 was assumed (Hofmann, Hart, 1978; Wadleigh et al., 1981)

NOTE: Sr stable isotope determinations were done by Prof. Dr. J.Burchart of the Geochronology Department, Institute of Geological Sciences, Polish Academy of Sciences in Warsaw

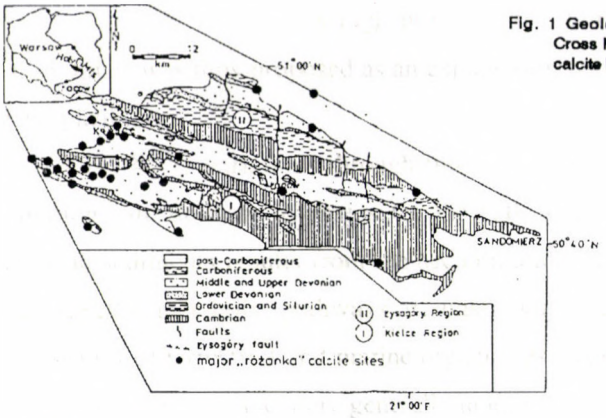

Fig. 1 Geologic map of the Holy Cross Mts. with main "rose-like" calcite locations.

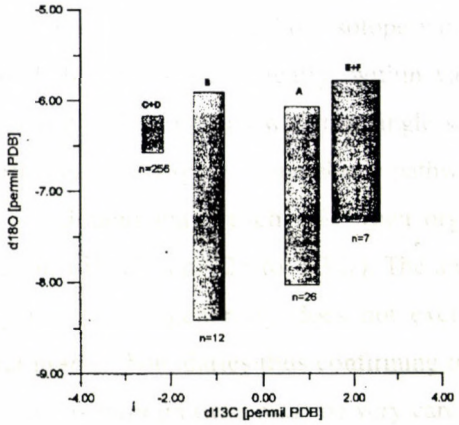

Fig. 2 Expected 95% ranges for mean values of $\delta^{13}C$ and $\delta^{18}O$ in four main phases of calcite mineralization from the Holy Cross Mts.
n - number of oxygen and carbon stable isotope determinations, phases A, B, C+D, E+F - refer to the text

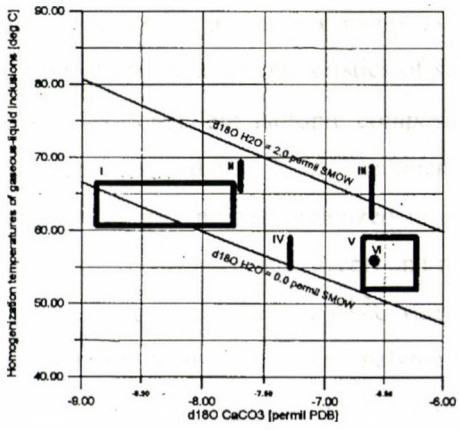

Fig. 3 Calibration curves for "rose-like" calcite from the Holy Cross Mts. derived from $\delta^{18}O$ determinations, and homogenization temperature measurements of gaseous-liquid inclusions. Samples (m - number homogenization temperature measurements, n - number of $\delta^{18}O$ measurements): I - Czernowa Góra (m=16, n=3), II - Chełsiowa Jama (m=12, n=3), III - Zelejowa Z/9 (m=7, n=1), IV - Zelejowa Z/6 (m=3, n=1), V - Zelejowa Z/17 (m=3, n=3), VI - Zelejowa Z/5 (m=1, n=1). For I, II and III the range of homogenization temperatures is given as expected 95% for a mean value.

New Automatic Techniques for D/H Measurement from Water and Organic Material

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Keywords: Equilibration, Pt catalyst, chromium reduction, H_2O, hydrogen, oxygen

The most prominent techniques for natural abundance D/H determination are reduction of water samples using either zinc in sealed tubes or uranium for sequential analyses. Neither of these methods allows a straightforward automation of the reduction reaction and integration with an isotope ratio MS for fully automated processing. In addition, the samples must be clean water. The hydrogen in the original sample of interest has to be converted to water before measurement. Due to the lack of automation it is difficult to avoid operator bias in the final results.

Techniques leaning more to automation are:

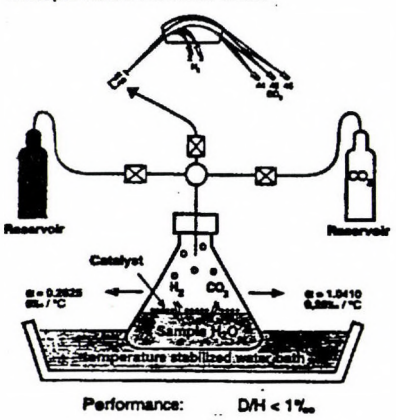
- Equilibration of water with hydrogen for H/D and CO_2 for ^{18}O determinations,
- Reduction of water and organic compounds using chromium at 850 - 950 °C for H/D determination.

Finnigan MAT in Bremen has invested into the above techniques and now offers fully automatic preparation lines integrated with the mass spectrometer. For the new HDO equilibration device, data will be presented that are routinely achieved on 4 ml water, for instance < 1 ‰ for H/D using Pt catalyst and < 0.04 ‰ for ^{18}O (Fig. 1, Tables 1 and 2).

Using chromium as a reduction reagent results will be shown for < 1 µl H_2O automatically measured to better than < 1 ‰ (Fig. 2, Table 3).

Results, used techniques, hardware requirements and calculations will be presented.

Fig.1
Automated determination of ^{18}O and $^{2}H(D)$ isotope abundances in water



H / Device

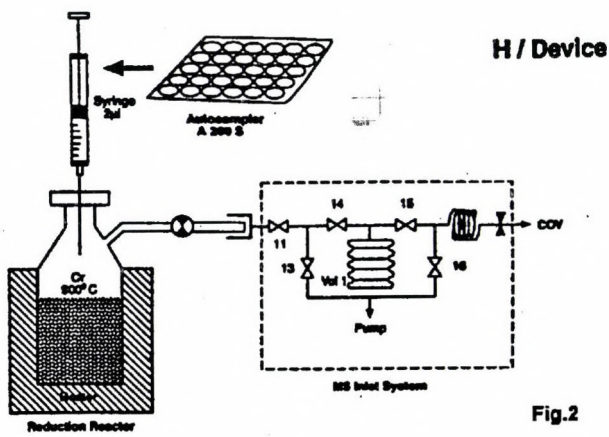


Fig.2

← HDO-Equilibrator

H_2O/HD Equilibration

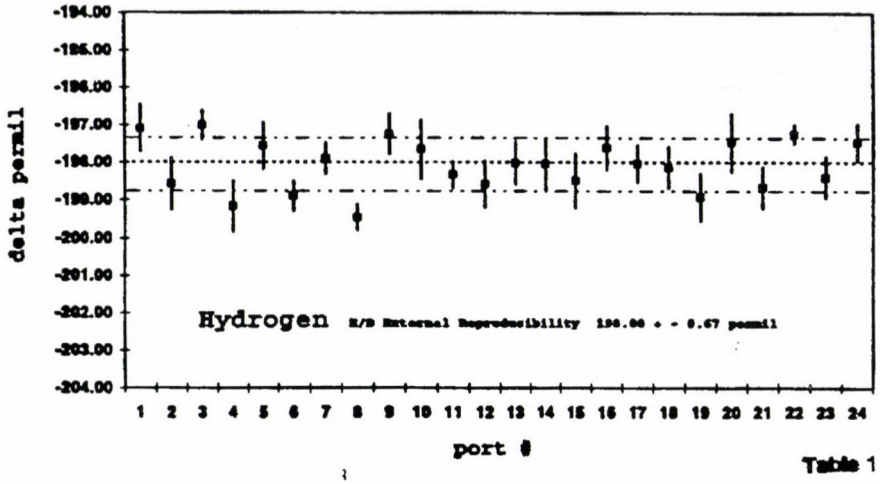


Table 1

H_2O/CO_2 Equilibration

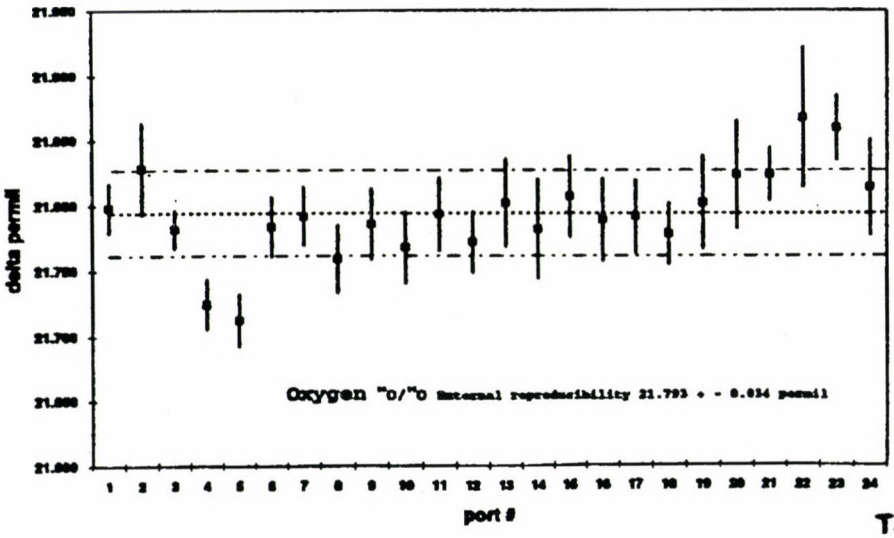


Table 2

Table 2: Summary of Chromium Reduction Data					
Compound	Delta vs work_std.	Delta vs Smow /raw	averages vs Smow /raw	std.dev.	Final Result vs VSMOW/SLAP
VSMOW	63.47	1.28			
VSMOW	62.63	0.49			
VSMOW	61.27	-0.79	0.11	0.84	0.00
VSMOW	61.18	-0.88			
VSMOW	62.74	0.59			
VSMOW	62.06	-0.05			
SLAP	-394.23	-429.66			
SLAP	-394.88	-430.27	-428.68	1.51	-428.00
SLAP	-391.91	-427.47			
SLAP	-391.74	-427.31			
GISP	-139.51	-189.83			
GISP	-139.72	-190.03	-190.99	1.23	-190.69
GISP	-141.94	-192.12			
GISP	-141.81	-192.00			
VSMOW	64.89	2.62			2.61
VSMOW	60.05	-1.94			-1.94
LSS	-116.86	-168.51			-168.24
LSS	-117.82	-169.41			-169.14
LSS	-121.10	-172.50			-172.23
WSO	382.70	301.84			301.36
WSO	382.52	301.67			301.19
SWS	66.00	3.66			3.65
SWS	65.69	3.37			3.36
bidest	-7.19	-65.25			-65.15
bidest	-7.33	-65.38			-65.28
HBW-1	6.14	-52.70			
HBW-1	9.12	-49.89			
HBW-1	7.66	-51.27	-51.47	1.05	-51.38
HBW-1	6.40	-52.45			
HBW-1	7.84	-51.10			
HBW-1	7.49	-51.43			
HBW-2	8.90	-50.10			
HBW-2	9.50	-49.54			
HBW-2	7.94	-51.00	-50.43	0.74	-50.35
HBW-2	7.87	-51.07			
MAT-A	9.75	-49.30			-49.22
MAT-A	9.60	-49.44			-49.36
MAT-B	5.83	-52.99			-52.91
MAT-B	7.10	-51.80			-51.71
WINEDEST.	-134.14	-184.78			-184.48
WINEDEST.	-134.03	-184.67			-184.38
URINE	50.89	-10.57			
URINE	46.59	-14.61	-12.37	2.06	-12.35
URINE	49.43	-11.94			
N-BUTANOL	-228.96	-274.05			
N-BUTANOL	-240.48	-284.90	-282.12	7.10	-281.68
N-BUTANOL	-243.16	-287.42			
SMOW	60.04	-1.95			
I-BUTANE	15.51	-43.88			
I-BUTANE	12.27	-46.93	-46.41	2.31	-46.33
I-BUTANE	10.69	-48.42			

Table3

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irm-GC/MS Used for Gas Applications

Keywords: irm-GC/MS, trace gas, N_2O, CH_4, CO_2, air, N_2, pre-concentration

Since the introduction of isotope ratio monitoring GC/MS (irm-GC/MS) the isotope ratio analysis of gases has become part of the research in a variety of applications.

On-line analyses with and without combustion are used. Various sample introduction techniques (Fig. 1), including pre-concentration (PreCon), ensure reproducibilities near natural abundance of < 0.2 ‰ for the determination of ^{13}C, ^{15}N and ^{18}O. Sample sizes range from 100 ml to less than 1 µl. Concentrations of compounds in the gas mixtures can vary from 100 % to less than 300 ppb (Table 1).

Direct analyses of all compounds in gas mixtures within a dynamic range of approx. 1:100 show reproducibilities close to the above value. Standard combustion conditions can be applied to combustible compounds in a gas mixture including methane.

A report will be given on the following applications:

- Determination of ^{13}C on natural gas from methane to n-pentane (Fig. 1)
- Measurement of $^{13}CO_2$ on smallest atmospheric gas samples (Fig. 2)
- Definition of the ^{15}N and ^{18}O isotope ratios on N_2O of air (Fig. 3a)
- ^{13}C isotope ratio determination on methane (1.7 ppm) of air (Fig. 3b)
- Sample transfer techniques (Fig. 4)

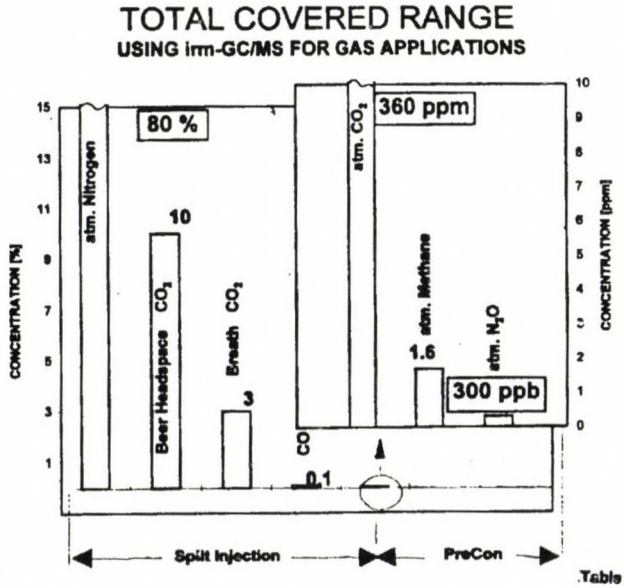

Table 1

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NATURAL GAS - SPLIT INJECTION

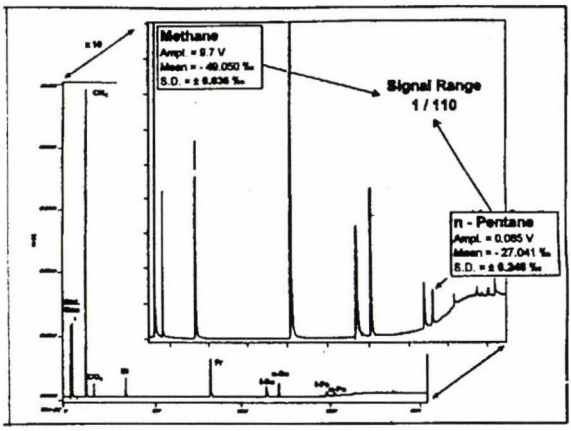
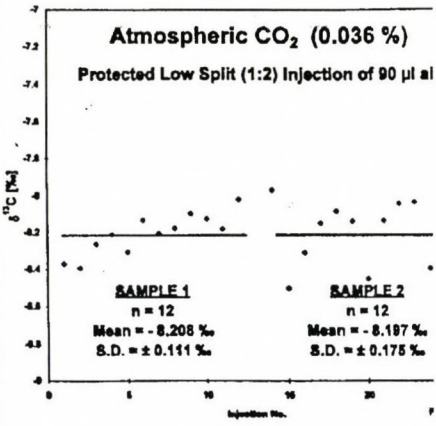
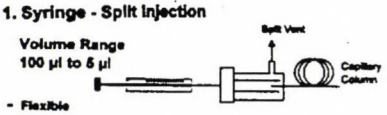


Fig.1



Sample Transfer Techniques

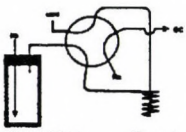
1. Syringe - Split injection



- Flexible
- Fast
- Contamination with air (=> Protected Mode)
- limited sample amount (not suitable for trace gases)

2. Loop Injection

- free of Contamination
- less flexible
- limited sample amounts (not suitable for trace gases)

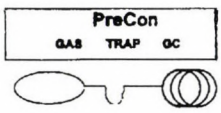


Purge Time Range

Sample Loop Range

3. Preconcentration - Loop Injection

- free of Contamination
- more flexible
- on-line sample clean up
- trace gases



Ranges :	Sample Volume	Purge Time	Freeze Time

Fig.4

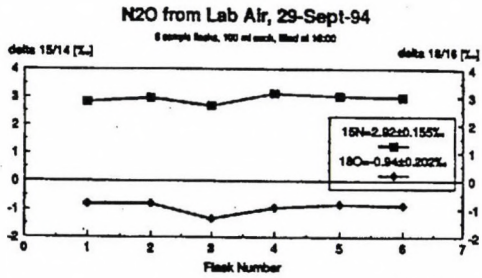


Fig.3a

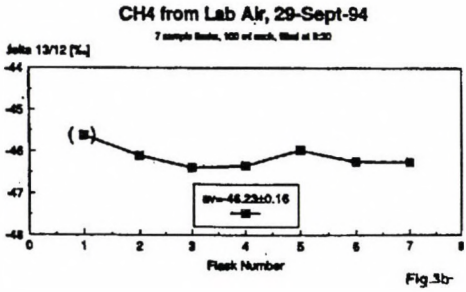


Fig.3b

Carbonate Equilibrium in Different Environments - A Stable Isotope Study

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Keywords: *marine, lake, sediment, carbon cycle, stable carbon isotope*

Introduction

The carbon cycle plays an important role in controlling many biological and chemical processes in marine and also in lake environments. It is extremely dynamic because of the abundance of carbon in different chemical forms that are labile to varying degrees: particulate organic and inorganic carbon, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC). The determination of the carbon isotopic composition ($\delta^{13}C$) provides a reasonably well defined measure of the contribution of carbon from the various sources, particularly that derived from organic matter. In this study we investigate the stable carbon isotope ratio - $\delta^{13}C$ of DIC - in order to define the processes affecting the production of dissolved inorganic carbon in different environments. Carbon added as CO_2 to the pore water can be derived from organic matter, the dissolution or precipitation of $CaCO_3$, and mixing with bottom water (Bauer et al., 1995, McNichol et al., 1991). While the isotopic composition of $CaCO_3$ usually differs little from bottom water, the isotopic composition of organic matter is very different, roughly 20‰ lighter. As a result, the $^{13}C/^{12}C$ ratio of DIC is very sensitive to the fraction of organic derived carbon in the CO_2 added during diagenesis. In highly reducing sediments, it has been found that the $\delta^{13}C$ of DIC can increase with depth in the sediments (Alperin et al., 1992, Blair et al., 1994). This increase has been related to the production of ^{13}C-depleted CH_4 in these sediments. As an end product in the degradation of organic carbon, methane is an important component in the carbon cycle of freshwater environments (Herzeg, 1988, Kuivila et al., 1988).

In this study, we present an investigation of the $\delta^{13}C$-DIC in pore water in two different environments (marine and lake) in order to define the sources of CO_2 to pore water and to understand the observed variations in $\delta^{13}C$.

Study sites

The marine samples were collected at station F in the central part of the Gulf of Trieste in the northern Adriatic. The sampling site is in a depth of 22m of water. It is composed of silty sand with up to 80% carbonate. The carbonates of biogenic origin are high Mg-calcite and aragonite and minor low Mg-calcite. Other minerals include quartz and clay, both detritial in origin. The sediment contains approximately 0.5% organic carbon. The composition of sediment in profile is practically uniform. The overlying water is oxic throughout the year, except in September 1995 when anoxic conditions were observed. The samples were taken only in June and September 1995.

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Lake sediments were taken in Lake Bled in Slovenia. The Lake is located in the NW part of Slovenia and has a surface area of 1.44 km^2 and mean depth of 18 m. It is strongly eutrophic with algal blooms. The water column is stratified most of the year, except during the early spring and autumn overturn. The bottom water temperature is nearly constant, between 4-8^{0}C. It has some natural inflows, but the most important is a pipeline inflow with fresh water from the Radovna river. At another site anoxic hypolimnical water is pumped out of the lake. The bottom layer below a depth of 15m is anoxic, but in some parts oxidising conditions prevail during most of the year. The sediment is composed of clayey silts with carbonate contents of 50-80% and is rich in organic carbon. In the uppermost layer from the western basin it reaches up to 10.7%. The samples were taken seasonally during 1995 from two different parts of the Lake from Zaka bay (where oxidising conditions prevail) and from the deepest part of the Lake where the environment is anoxic.

Methods

Sediment samples were taken by SCUBA diving, inserting a Plexiglas tube directly into the sediment. Lake sediments were taken using a gravitational corer with a Plexiglas tube. Samples were transported to the laboratory within 4 hours of collection. In a N_2-filled glove bag, the cores were cut into 2 to 4 cm segments. Pore water was squeezed from the sediment under 0.4 MPa nitrogen through a 0.45 μm membrane filter. Immediately the pH, alkalinity and δ^{13}C-DIC were measured. Alkalinity was determined with potentiometric titration by the method in an open vessel (precision ± 1%). Samples for δ^{13}C-DIC analysis were introduced to evacuated exetainers containing 100% H_3PO_4. Total CO_2 was sparged, collected and the isotopic ratio was measured on a Europa 20-20 ANCA-TG mass spectrometer. The sediment where δ^{13}C of organic carbon was determined was first dried, then acidified with the addition of 3N HCl to remove carbonates. The redried sample was combusted and the resulting CO_2 was measured on a Europa 20-20 ANCA-SL mass spectrometer. Samples of sediment and biogenic carbonates were first cleaned and then roasted at 375^{0}C for an hour in vacuo. Carbon and oxygen isotopes were measured in the CO_2 gas released by reacting with 100% phosphoric acid for two hours at 50^{0}C. The isotopic analyses were performed on a Varian MAT-250 mass spectrometer. All isotopic measurements have been referenced to the PDB standard and expressed in ‰. The precision of the measurements for δ^{13}C and δ^{18}O values was ± 0.05‰ for carbonates, and 0.2‰ for δ^{13}C-DIC and organic carbon.

DIC was determined from pH and alkalinity measurements after Millero (1995) where dependence on temperature and salinity was taken into account. The anion analysis of pore water (SO_4^{2-}, S^{2-}, PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+), were performed through standard spectrophotometric methods. Metal concentrations were determined using flame AAS (Ca^{2+}, Mg^{2+}, Fe_{tot}, Mn_{tot}).

Results and discussion

Marine environment. The values δ^{13}C-DIC vary between -2.36 and +2.9‰. To estimate the contribution of carbon from organic carbon oxidation and from calcite dissolution the isotopic composition of bulk carbonate and organic carbon was

measured. The $\delta^{13}C$ of both changed little with depth; the average $\delta^{13}C$ value is +1.02‰ for carbonate and -21.9‰ for organic carbon (typical for the majority of marine sediments). In general, the oxidation of organic matter will decrease the $\delta^{13}C$ of DIC. It was found from the negative correlation between $\delta^{13}C$ and DIC that oxidation of organic matter is an important process in these sediments. We calculated that the flux of DIC was enriched in ^{13}C over that expected from the stoichiometric oxidation of Redfield organic matter. This enrichment was found even after $CaCO_3$ dissolution was accounted for. There are some possibilities to explain this observation. A significant amount of CO_2 may be produced from the dissolution of carbonate. From the calculated saturation state there is evidence that conditions are favourable for dissolution, but a significant increase in dissolved Ca^{2+} was observed only in June. Calculations showed that the dissolution of $CaCO_3$ was not responsible for ^{13}C-enrichment. Thus the enrichment must be due to fractionation during organic matter oxidation or to isotopic exchange with bottom water. Other investigations (McNichol et al., 1991) suggest that more probably the diffusion of bottom-water carbonate ion into pore water or the diffusion of ^{13}C-depleted H_2CO_3 from pore water to bottom water or the production of DOC (dissolved organic carbon) are responsible for the isotopically heavy values. In fact the first measurements of isotopic composition of DOC in pore water show more negative values of $\delta^{13}C$ (-26 to -23‰), but further studies are necessary to distinguish between these mechanisms.

Lake environment. To estimate the influence of organic carbon in the carbon cycle in the Lake the isotopic analysis of sedimentary organic carbon was performed. The values of $\delta^{13}C$ vary widely between -27 and -38‰ and increase regularly with depth. Generally, in the deeper parts of the lake the values are lower, due to methanogenic bacterial populations in the sediments (Freeman et al., 1990). $\delta^{13}C$-DIC displays a positive gradient of +26‰ from bottom water to 40-cm depth. In the upper profiles the values are similar to that of overlying bottom water, but deeper in the sediment the values of $\delta^{13}C$-DIC increase. The contribution of carbonate could not explain this enrichment, since the $\delta^{13}C$ of autigenic carbonates are between -4 and -2‰, so this enrichment should be caused by methane production. According to its isotopic composition, methane forms via acetate fermentation. Methane production should not occur in the upper 15 cm of the sediment. Therefore it must diffuse from the underlying methanogenic horizon and be oxidised in the sediment column. We observed a significant increase of NH_4^+ and S^{2-} concentration at the same depth interval. The lower pH caused the dissolution of carbonates.

Conclusion

In marine sediment, decomposition of a large quantity of organic matter leads to sulphate reduction. This study suggests that the enrichment of $\delta^{13}C$-DIC could be explained by the diffusion of bottom-water carbonate ions into the sediment, the diffusion of H_2CO_3 from pore water to bottom water or by the production of DOC. Further investigations are needed to prove their influence in the ^{13}C-enrichment of DIC.

In lake sediment, reactive organic matter is decomposed to methane in the sediment column. It was found that values of $\delta^{13}C$-DIC in pore water in upper profiles are similar to values of overlying bottom water. Deeper in the lake sediments the DIC is heavier due to fractionation during methanogenesis. In the anoxic part of the lake a

pronounced increase in the δ^{13}C-DIC was observed immediately below the sediment-water interface.

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Localization and quantitative estimation of leakages in big water reservoirs and dams

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Keywords
Leakages, dams, water reservoirs, tracer methods, gold-198, indium-113

Leakages from hydroengineering buildings presents a serious problem from the point of view of both safety and economics.
The radiotracer sorption method for localization of such leakages in dams and big artificial water reservoirs has been developed at the INCT [Owczarczyk1983]. The method have been successfully applied for examination of leakages in several big objects in Poland.
The principle of the method is shown in Fig. 1.
Method consist, in general, in the introduction into the water of a radiotracer characterized by permanent sorption on a material in the bottom or watertight screen of the reservoir examined. The water flow towards the place of leakage entrains a tracer. Its particles are deposited by sorption on surfaces surrounding the place. Radioactive spots so formed in areas where leakages take place are located thereafter by means of special detection equipment. Of the tested radioisotopes the following appeared to be most suitable for the purpose as they have the best sorption characteristics in respect of typical materials used in large water reservoirs such as sand, concrete, asphalt concrete etc. They are: ^{113m}In obtained from the Sn/In generator in the form of $InCl_3$ solution and ^{198}Au in the form of colloidal solution of metallic gold. A radioactivity of 37-75 MBq (1 to 2 mCi) is quite sufficient to label about 4 m^2 of the examined section.
According to opinions of hydraulic engineers and operation experts the proper evaluation of operational safety of dams and other large hydraulic structures, as well as forecasting of imminent filtration phenomena, require proper knowledge of the leakage intensity [Ryżak 1982]
The proposed method is based on the balance of the radiotracer adsorbed on the bottom around the leakage.

$$VC_v = QtC_v = C_s s \qquad (1)$$

where:
Q - leakage rate [m^3/s],
V - local leakage volume [m^3] during time t[s] of tracer cloud - bottom interaction,
C_v - mean concentration of the tracer in the cloud [Bq/m^3],
C_s - mean surface activity of the tracer [Bq/m^2],
s - leakage area [m^2].

$$n_s = n_s' \exp(\mu L m) \qquad (5)$$

where:
μ - radiation absorption coefficient for the given material [m^{-1}],
n_s' - recorded local surface counting rate [cps].
Finally, the formula takes the following form:

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$$Q = \frac{\alpha_s H \exp(\mu L m) \int_0^{\infty} \int_0^{\infty} n_s' dx dy}{\alpha_v t \int_0^{H} n_v dz} \qquad (6)$$

The above formula was subject to verification in laboratory conditions in a hydraulic flume specially designed for leakage simulation. The tracer used was In-113m obtained from a Sn/In generator. The sorption characteristics of the tracer were determined in a filtration column. The Table 1 shows the results of verification experiments for sandy bottom conditions.

The presented results indicate good agreement of the experimental data with the adopted calculation procedure, this forming a basis for further development of the method in the way that would make it suitable for investigations on large scale hydroengineering objects.

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Table 1. Results of verification

Q measured litres/min	Q calculated litres/min	Error %
0.7	0.62	11
1.67	1.18	29
1.97	1.36	30
2.47	2.35	8

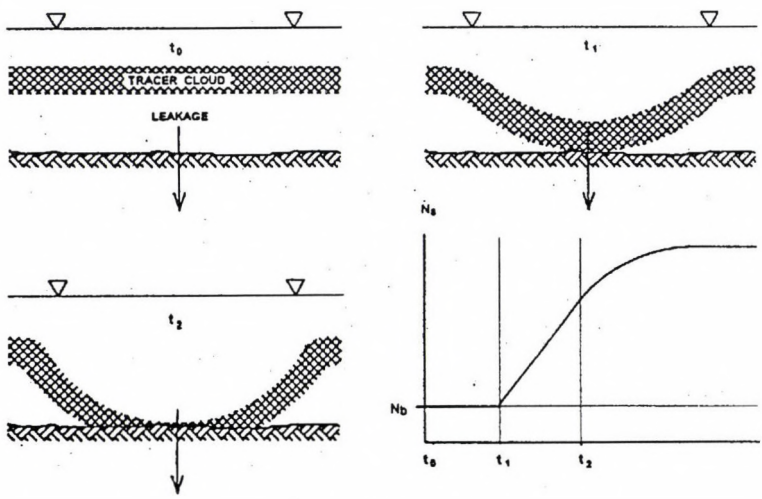

Fig. 1 Principle of the method.

The mean values of surface tracer concentration and concentration of the tracer inside the cloud are defined as follows:

$$C = \alpha_s N_s = \alpha_s \int_0^{\infty}\int_0^{\infty} n_s dxdy \qquad (2)$$

where:

α_s - detector calibration coefficient for the measurement of the bottom surface contamination [Bq/m^2 cps],
n_s - local counting rate around the contamination spot on the bottom [cps],
N_s - mean surface counting rate [cps],
x, y - length and width co-ordinates [m],

and:

$$C_v = \alpha_v N_v = \alpha_v \frac{1}{H}\int_0^H c_v dz = \alpha_v \frac{1}{H}\int_0^H n_v dz \qquad (3)$$

where:

α_v - detector calibration coefficient for the measurement of the tracer concentration inside the cloud [Bq/m^3 cps],
c_v - local tracer concentration inside the cloud [Bq/m^3],
n_v - local counting rate inside the cloud [cps],
N_v - mean counting rate in the cloud [cps],
H - thickness of the tracer cloud [m],
z - depth co-ordinate [m].

Calibration coefficients α_v and α_s have been specified for each detector used under laboratory conditions.
The integral in equation (3) defines the activity distribution over the cloud thickness.

Hence:

$$Q = \frac{\alpha_s N_s}{\alpha_v N_v t} = \frac{\alpha_s H \int_0^{\infty}\int_0^{\infty} n_s dxdy}{a_v t \int_0^H n_v dz} \qquad (4)$$

Usually the radioactive tracer interacting with the permeable surface of the bed forms a contamination layer of a certain thickness and tracer concentration distribution. This requires the introduction of a correction factor into the formula (4) that would take into account the radiation absorption by the effective layer L_m [m] of the bed material:

ISOTOPE DILUTION ANALYSIS (IDA) TECHNIQUE FOR DETERMINATION OF IODINE IN SEVERAL WATER SAMPLES

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Keywords: iodine-131, iodine, isotope dilution analysis (IDA), determination of iodine, iodine in water.

INTRODUCTION

The analysis of environmental samples for trace amounts of iodine has become of renewed interest, since this element is considered to be potentially important for man. The trace element iodine is ubiquitous in the human environment. Iodine compounds are important in organic chemistry and very useful in medicine. Twenty-three isotopes are recognised. Only one stable isotope, iodine-127, is found in nature. Lack of iodine is cause of goitre.

Various useful analytical methods using radioactivity have been developed in the region of the analytical chemistry. Theoretical and experimental investigation on isotope dilution analysis (IDA) methods have been reported. Isotope dilution analysis is the most useful of the indicator radio analytical method, especially for elemental analysis. New concepts of IDA, such as substoichiometric and sub-super equivalence IDA, have improved the sensitivity and expanded the applicability of the method for trace analysis (Lesny et al, 1990; Singh and Gars, 1994). IDA has been used for the analysis of biological and geological materials, water, soils, semiconductors, etc. (IAEA Report, 1986). Because of the high sensitivity of radioactive tracers isotope dilution analysis presents a suitable method for the determination of volumes and amounts of substances. Also this method can be applied for the accurate measurement of the isotopes of iodine in biological fluids of interest in human metabolic studies.

A simple and rapid method (IDA) has been used that allows the determination of trace amounts of iodine in water samples, because of the goitre prevalence in iodine-deficient regions.

The term endemic goitre is used when more than 10% of the population or 5% of an adolescent group have goitre. Non endemic regions with only sporadic cases of goitre show very low percentage of non toxic goitre. In the endemic regions, the 24 hours urinary iodine excretion is less than 50 to 80 Mg. Endemic regions are Central Europe, Finland, and large areas of Central Africa. Non endemic regions include for example, the United States, Great Britain, Sweden and Norway (Biersack and Grünwald,1995). Also endemic areas in Western Anatolia-Turkey are Manisa, Demirci, Ödemiş and Mugla.

The purpose of this work is to demonstrate the use of isotope dilution analysis for the determination of trace amounts of iodine in several water samples (tap, drinking, ground, thermal and spring water). It is assumed that the obtained data will be valuable on a public health study.

EXPERIMENTAL

The fundamental procedure is described (Möbius,1988; Ehmann and Vance,1991) with the principle of IDA.

Reagent:

Radionuclide iodine-131 ($t_{1/2}$= 8 d, E_γ= 364 KeV) was supplied from Ege University, Faculty of Medicine, Department of Nuclear Medicine. All reagents were analytical reagent grade.

Procedure:

According to the required procedure the centrifuge tube containing the iodine-131 activity in 1 ml NH_4OH (conc.) is measured for activity in a well-type NaI (Tl) scintillation detector. A definite amount of analyte mixture (0.1 M, about 1.0 ml) is added. After intimately mixing Ag+ is precipitated with 1.0 ml $AgNO_3$ (0.1 M) solution. Some $NaNO_3$ (solid) is added and the mixture is heated in the water bath for about 10 min. After the solution is filtrated, the supernate discarded and precipitate washed with NH_4OH (1 M).

The net rate of the remaining AgI precipitate is determined. The amount of iodine present in the text solution by using the equation was calculated.

$m_a = (A_1/A_2 - 1)m_1$

m_a= Unknown mass

A_1= Activity of added indicator

A_2= Activity of sub product

m_1= Amount of sub product

As low as 0.00127 mg of iodine in 1 ml aqueous solution could be determined by the proposed method.

Calibration:

A series of solutions containing 1.27-0.00127 mg of iodine in KI were prepared. The values were computed and plotted. The least squares regression analysis was used for the processing of experimental data (Fig.1). Unknown amount of iodine in the solution was calculated.

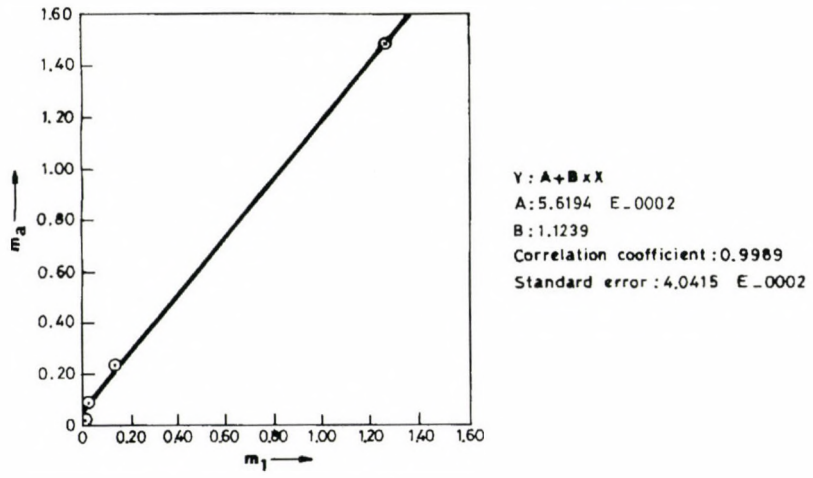

Figure 1. Calibration curve.

CONCLUSION

Our results clearly prove that by the IDA method reliable analytical results can be obtained in the determination of iodine in several water samples. The proposed radiometric method can be compared very well with spectrophotometric titration, spectrophotometric method (Pasevento

and Profumo,1985; Peker,1992) in terms of sensitivity, selectivity and duration of experiment. Results of analysis of the water samples for iodine content by IDA are shown in Table 1.

The proposed method can be successfully and more easily applied for routine work.

Table 1. Iodine content of the water samples

Sample No.	Iodine mg/ml
1	0.73
2	0.57
3	0.53
4	0.44
5	1.36

(Sample No 1: Drinking water, No 2: Ground water, No 3: Thermal water, No 4: Tap water, No 5: Spring water)

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On Use of Hyalophane for K-Ar Dating in the Central Bosnian Schists Mts.

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Key words: Isotope geochronology, K-Ar dating, ammonium hyalophane, activation energy, closure temperature, retrogressive metamorphism, Central Bosnian Schists Mts.

After the first report on discovery of the subvertical, alpine, quartz-hyalophane veins, wide up to 25 cm, close to the village Busovača, Central Bosnia, within the low-medium metamorphic rocks of the Inner Dinarides (Fig. 1) by Divljan and Simić (1954), a number of mineralogical studies on their mineral load, quartz, hyalophane, anhydrite, pyrite, anatase, rutile, hematite, apatite and albite has been published. The huge waterclear, up to 10 cm in diameter, large hyalophane crystals, weighing close to 5 kg, however, were the matter of special attention (Barić, 1955, 1969; Zebec, 1980/81; Bermanec, 1992; Beran et al., 1994; Palinkaš et al., 1995).

An unusual Cr-Ba-Fe-Cu stratabound mineralization in the same chlorite-muscovite-quartz schists, quartz-sericite schists, locally quartz-graphite schists and restricted lenses of subgraywacke metasediments, and amphibole-tremolite or tremolite-sericite schists (orthometamorphics, Mayer, 1991), is cut almost perpendicularly by quartz-hyalophane veins. Its mineralogy, magnetite, zincian chromespinel, ferrichromite, pyrite, chalcopyrite, enargite, bornite, siegenite, siderite, quartz, albite, hyalophane, muscovite, chromium-chlorite and mangoan ankerite, has been described by Jurković et al. (1992), Jurković and Jakšić (1994) in detail.

Hyalophane, (K,Ba)[$AlSi_3O_8$] is a solid solution of celsian and adular (orthoclase) with some albite components. The Bosnian hyalophane, together with its exceptional size, bears some unusual crystallochemical characteristic, 10-20 % of albite and 1 % NH_4^+-component (the first record of NH_4-containing hyalophane, Beran et al., 1992). The average sample contains (in %): SiO_2 - 49.88, Al_2O_3 - 22.43, FeO - 0.05, BaO - 18.52, Na_2O - 1.44, K_2O - 6.87, TiO_2 - 0.08, NH_4^+ - 0.10; Summ: 99.33 (Bermanec, 1992).It appears in huge euhedral, prismatic, pseudo-orthorombic crystals with regularly grown faces, (110), (010), (001) and (201). Manebach twins appear seldom, Baveno twins have been noticed but always with the

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common Manebach-Baveno fourlings twins. Carlsbad twins and Cunnersdorf twins have been observed as well (Zebec, 1987/88).

Hyalophane is rich in H_2O-NaCl-CO_2 fluid inclusions, often with rutile and some anysotropic daughter minerals. Solid inclusions of hematite, chlorite and other opaque daughter minerals are common (Palinkaš et al., 1995). Microthermometric measurements revealed following data: $T_{FM}CO_2$, - 60.0 °C to -57,2 °C; $T_{LM}CO_2$ -58.1°C to - 56.5 °C; T_{LM}Ice, -11.7 °C to - 4.0 °C; T_{LM}Clath +2.5 °C to + 6.2 °C; T_HHCO_2 (homogenization), +14.6 °C to + 29.2 °C; T_HTOT, 320 °C. Concentration of NaCl in wt. % NaCl equ., 6.6 - 13.5 %; CH_4 (0.55 - 8.8 %). Pressure at the homogenization temperature in inclusions is estimated at 2250 bars, what appropriates to 8.5 km. Micro Raman spectroscopy recognised CO_2, H_2O, N_2, presence of NO_2-group, and carbonates as daughter minerals.

Hyalophane is formed from metamorphic fluids during the retrograde metamorphism in the open fractures at already brittle rock conditions. The passive continental margin of Apulia, where Busovača region belongs, encounters several thermal and metamorphic events, but this one seems to be the last.

The time of the retrograde metamorphism was determined by dating the K-rich minerals, muscovite and hyalophane, that were formed during this process. Muscovite, that crystallised together with the hyalophane and is present in the hyalophane veins resulted 38.7 ± 1.6 Ma, whole rock samples from the vicinity of the hyalophane veins yielded 38.6 ± 1.5 Ma and 40.3 ± 1.6 Ma. The concordant ages support the assumption that K in the country rock is hosted mostly by the white micas. Microthermometric measurements determined 320 °C for the mineralization (Palinkaš et al., 1995), this value is near to the well established closure temperature (350 °C, Purdy and Jäger, 1976) for muscovite, therefore the white micas were closed at the time of their formation and the time span of 40.3 - 38.6 Ma can be accepted for the age of mineralization. 3 hyalophane samples resulted younger ages from 25.3 Ma to 16.7 Ma. The most likely explanation of this bias is argon loss from the hyalophane caused either by rearrangement of the mineral structure or by weaker argon retentivity.

Argon extraction experiments were performed on the oldest and youngest minerals, and the results were plotted on an Arrhenius diagram (Fig. 2). Activation energies of 32.9 kcal/mol and 35.2 kcal/mol have been deduced from the fitted lines and closure temperatures were calculated according to Dodson (1973). Assuming a cooling rate of 10 °C/mill. year, 189 °C and 214 °C closure temperatures were obtained for the two minerals. Assuming 8.5 km for the

depth of mineralization and uniform uplift of the area, 0.12 -0.27 mm/year is obtained for the uplift rate.

This model is regarded only as a first approximation. It explains the reduced age values of hyalophanes, but understanding the real process of argon release needs further investigations. Namely, the Arrhenius diagram (Fig. 2) suggests, that argon release was controlled by two activation energies. In this case a unique value for the closure temperature can not be used, and the K-Ar age is influenced by the distribution of radiogenic argon atoms in the sites of different activation energies. Moreover, the structure of hyalophane crystals may also change during their history. There are some indications on the existence of a hypothetical Ba-molecule analogous to the Schwantke molecule at high pressures and temperatures which presumes mirmekitization likewise to microcline-quartz intergrowth (Bermanec, 1992). This may cause argon loss and also the redistribution of argon atoms in the sites of different bounding energies. Unfortunately, our investigations performed up to now are insufficient for the determination of different activation energies.

At the present state of our study we may state, that hyalophane is more susceptible to secondary heat effects than white micas, and its K-Ar age (together with crystallographic data) can be suitable for timing low temperature processes.

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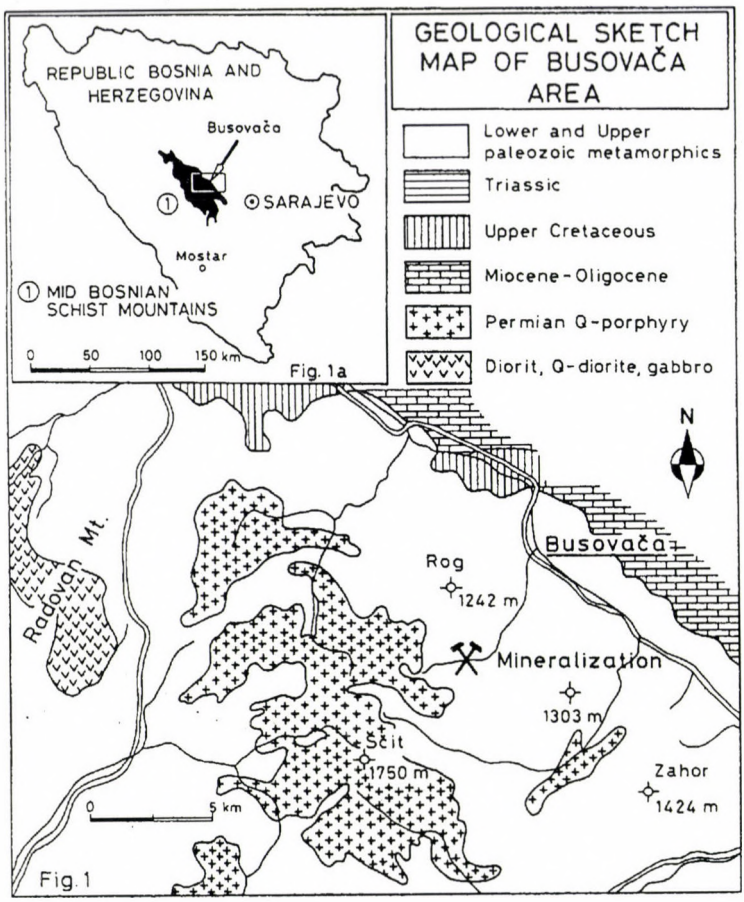

Fig. 1
Geological sketch map of Busovača area

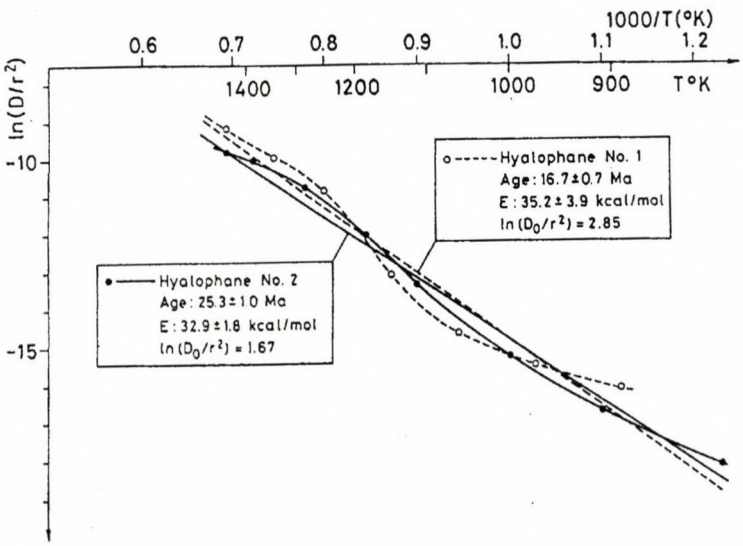

Fig. 2
Arrhenius diagram for Ar release from hyalophane

FIRST COMPARISON OF THE GAS PROPORTIONAL COUNTERS AND LIQUID SCINTILLATION SPECTROMETRY USED IN THE GLIWICE RADIOCARBON LABORATORY

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Keywords: radiocarbon, liquid scintillation beta spectrometry, gas proportional counters

Radiocarbon method started in Poland at Poznan University in the beginning of fiftys (Moscicki, 1953).
At first Geiger-Müller counters was used filled with CO_2 and CS_2 mixture. After removing Moscicki's laboratory to the Gdansk University begun works on using CO_2 filled proportional counters for radiocarbon dating (Zastawny, 1966).
Few years after that Radiocarbon Laboratory moved together with its staff to the Silesian Technical University in Gliwice (Pazdur, 1995). Routine radiocarbon dating started at the Gliwice Radiocarbon Laboratory in the early seventies. Successively done development brought us four measurement systems. Three of them are single proportional counter with anticoincidence Geiger-Müller shield and passive - material shield. Fourth system consist of three small proportional counters guarded by one anticoincidence and one passive shields (Moscicki, Zastawny 1977; Pazdur, Pazdur, 1986; Pazdur, Walanus, 1986; Goslar 1990). It is very important to notice that in eighties gas proportional counters was the most popular radiocarbon technique used in dating. It was because of the well stability on reasonable low background (Mook, 1983).

Eighties brought to the radiocarbon dating commercial liquid scintillation spectrometers with good long and short term stability, designed specially for low level work. (Polach et al, 1984; Polach, 1987; Polach, 1989; Polach, 1992; Kajola et al, 1984; Kajola et al, 1985; Cook et al, 1990).
In 1994 Gliwice Radiocarbon Laboratory got one of the best LS spectrometer Quantulus. It was due to IAEA Technical Cooperation Programme Project POL/8/-12. In the same year began works on the spectrometer calibration for radiocarbon dating in different counting geometries (Pawlyta et al, 1996).

There are few factors that can be used to compare radiocarbon measurement systems (Theodorsson, 1991). First is B - background counting rate, second one is S_0 - modern standard (Stuiver, Polach, 1977) counting rate. Third one is so called factor of merit which is defined as:

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$$FOM = \frac{S_0}{\sqrt{B}}.$$

FOM is very useful for comparing systems when counting samples of activities close to background. Next factor is maximum determinable age, which should be found using equation:

$$T_{max} = 8033 \ln(\frac{S_0\sqrt{t}}{2\sqrt{2B}}),$$

where t is counting time in minutes.

Tab.1. Gas proportional systems at Gliwice Radiocarbon Laboratory, t=1000min used in Tmax and Tmin calculations.

System name	mass of carbon [g]	B [cpm]	S_0 [cpm]	FOM	T_{max} [B.P.]
L1	3.2	7.436 ± 0.014	35.723 ± 0.024	13.1	40000
L1	1.6	6.333 ± 0.012	17.878 ± 0.015	7.1	35100
L2	4.5	5.664 ± 0.009	48.229 ± 0.035	20.3	43500
L3	0.8	2.734 ± 0.014	9.094 ± 0.024	5.5	33000
L4		1.086 ± 0.007	1.619 ± 0.014	1.6	22900
L5		1.020 ± 0.009	1.607 ± 0.008	1.6	23100

Tab.

2. Liquid scintillation beta spectrometer Quantulus at Gliwice Radiocarbon Laboratory, t=1000min used in T_{max} calculations.

Counting geometry	mass of carbon [g]	B [cpm]	S_0 [cpm]	FOM	T_{max} [B.P.]
2ml	1.62	0.252 ± 0.007	12.393 ± 0.047	24.7	45100
3ml	2.43	0.357 ± 0.008	20.795 ± 0.055	34.8	47900

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PALEOENVIRONMENTAL ISOTOPE RECORD IN THE FRESHWATER CARBONATE SEDIMENTS

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Keywords: tufa, speleothems, lake sediments, stable isotopes, radiocarbon, Holocene, caves, Poland

Isotope paleoenvironmental studies have been performed during the last about 10 years. They were based on the stable isotopes and radiocarbon concentration measurements in the freshwater tufa, speleothems and lake sediments. The field of the researches contains the Polish and Slovac region: Cracow Upland, Polish and Slovac Carpatians and the Gościąż Lake and its environs (Central Poland).

Calcareous tufa

Measurements of isotopic composition of carbon and oxygen (including ^{14}C activity, $\delta^{13}C$ and $\delta^{18}O$) were performed on the tufa samples from five sites in the southern Poland (Pazdur *et al*, 1988a).Because of complexity of investigated physical system, which is described by great number of correlated geochemical and biological factors, an attempt to determine the relation between the value of apparent age and the isotopic composition of carbon and the type of calcareous tufa sediment is based simply on statistical analysis of experimental data.

Investigated profiles of calcareous tufa sediments as characterized by either constant or variable value of the apparent age. Analysis of corelations between ^{14}C age of tufa sediments and measured values of $\delta^{13}C$ in the studied profiles indicate that constant value of apparent age is observed in profiles with constant (within limits of experimental errors) values of $\delta^{13}C$. In profiles with variable value of $\delta^{13}C$ the value of apparent age cannot be regarded constant.

It was found that the relation between the value of apparent age and isotopic composition of carbon is not equivocal, and is finally determined by the type of tufa sediment. On the basis of obtained relation between mean value of apparent age and mean composition of carbon in calcareous tufa profiles with constant value of apparent age, definite of criteria have been formulated, wich specify condition of ^{14}C dating of tufa profiles without organic matter (Pazdur, 1988b).

Age calcareous tufa from profiles which reveal variable value of apparent age and do not contain layers with organic matter may be, in certain specific cases, estimated by comparision with profiles with known value of apparent age and similar isotopic composition of carbon.

Results of investigations of isotopic composition of oxygen in recently desposited calcareous tufa, indicate serious violation of isotopic equilibria during the process of tufa sedimentation. Talking into account experimently determined magnitude of the kinetic effect and actually observed depedance of isotopic composition of oxygen in meteoric water in Cracow Upland area upon temperature, the changes of mean annual temperatures in southern Poland were estimated in time interval from about 9500 BP to 2000 BP (Pazdur *et al*, 1988c). Reconstruction of Holocene paleotemperatures is based on several simplifying assumptions. Comparison of estimated oxygen isotopic paleotemperatures with the results of other methods leads to conclusion that both the estimated values of mean annual temperatures and their time changes reflect characteristic thermal changes during the Holocene, confirming therfore the validity of this approach.

Speleothems

For this project, we chose to study speleothems deposited in caves of the Cracow - Wieluń Upland, the largest and best-explored karst region in Poland , extending from Cracow in south to Wieluń, *ca.* 160 km north of Cracow. The Cracow - Wieluń Upland consist of Upper Jurassic limestones and covers *ca.*2990 km^2. More than 1000 caves are located in this area. Most of the caves are relatively small; only two are longer than 500 m and 66 longer than 100 m. Many caves were inhabited during the Middle and Upper Paleolithic and then during the Mesolithic and Neolithic.

A group of older ^{14}C dates, obtained on speleothem samples from 18 caves range from 45 to 20 ka. This time frame, determined by the presence of speleothems, coincides almost exactly with interval of the Interplenivistulian. An interruption occured in speleothem formation between 20 and 10 ka BP, caused by serious climatic deterioration associated with the last glacial maximum. The younger dates span the Holocene, the broad maximum falling within the Atlantic phase.

^{14}C, U/Th and AAR (amino acid racemization) dates were obtained from Wierna Cave. These, accompanied by $\delta^{13}C$ and $\delta^{18}O$ values obtained along of its growth line indicate a rapid cooling before speleothem JWi2 stopped growing (*ca.* 18 ka BP, Pazdur *et al* 1995a).

The massif of Slovak Karst situated in the Bodwa river basin south of Slovak Rudawy is one of the largest karst region in Europe. The area of limestone rocks occuring at surface exceeds 600 km^2 and the number of knows caves exceeds 500. In the southern part of the area the outcrops of Mesosoic base units are dominating. Mesosoic rocks are in same places overlain with flysh sedimentary rocks of Paleogene age. In southern part of the area there is a continuous transition from Miocene marine sediments to lower Pliocene sediments.This study was confined to four caves located on Plesivecka Planina and Silicka Planina in the central part of the Slovak Karst (the caves Diviaca, Salanka and Zakrutowa). The results obtained with the radiocarbon and TL/ESR methods of dating are compared with the available global paleoclimatic records and used for reconstruction of selected elements of the study area during the last 300 ka (Pazdur *et al*, 1995b).

Lake sediments

Gościąż Lake, situated in the Płock Basin, Central Poland, is the largest and deepest in the system of the four " Na Jazach" lakes. The significance of this lake was recognized immeditately after discovery of its laminated sediments consist of carbonaceous-sulphuric gyttja with a large amount of iron and other elements, accumulated in a superaqueous environment dominated by reduction processes. The sediment reveals distinct lamination, consisting of *ca.* 12,500 laminae couplets, extending back from the present to the Allerod interstadial. Varve chronology and AMS dates on macrofossils from Gościąż Lake were used to determine the duration of the Younger Dryas.

Radiocarbon and stable carbon isotope ratios have been measured in organic and carbonate fractions of laminated of the Gościąż Lake (Pazdur *et al*, 1994). Parallel varve counting in four cores taken from the deep central part of lake have lead to development of an independent varve chronology which may be compared with results of radiocarbon dating. Comparison of measured ^{14}C activities in carbonate fractions of lake marl with varve ages allow for the accurate estimation of secular changes of the ^{14}C dilution factor of total dissolved inorganic carbon. Using the geochemical model and reconstructed changes of ^{14}C dilution it has been possible to reconstruct mean lake level during the Lateglacial and Holocene. The result of model calculations are compared with an idependent record of lake level changes deduced from ^{14}C dated lithological boundaries marking low and high lake stands in numerous cores taken along lake shores, as well as with lake level data available from southern Sweden and France (Pazdur *et al*, 1995c). Obtained patterns of lake level fluctuations show remarkable

with behaviour of Swedish Lake during the last 12 ka BP reflects global climatic changes fairly well.

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ANTHROPOGENIC CHANGES OF THE ISOTOPIC COMPOSITION OF ATMOSPHERIC CARBON IN UPPER SILESIA

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Keywords: radiocarbon, environment, Suess effect, Upper Silesia, tree–rings

Carbon is an element abundantly present in the environment. It can be found in pure form or in many components in the atmosphere, biosphere and water environment on the Earth. The concentration of carbon and its isotopic composition, are different in different environments and change in different geochemical reservoirs. These changes are natural, and have their origin in astrophysical, geophysical, biological and other systems. The natural equilibrium of radiocarbon in the atmosphere and oceans, has been disturbed during the last century by a large injection of both stable and radioactive isotopes of carbon. There are three main processes that cause important changes of radiocarbon concentration in the contemporary environment. The first process is associated with the systematic increase of fossil fuel combustion. The increasing amount of "dead" carbon dioxide causes a decrease of radiocarbon concentration. This effect is global, but may also be observed locally in industrial areas. Large amounts of artifical radiocarbon in the atmosphere were produced by nuclear weapon tests. The maximum increase was noted in 1963, when the radiocarbon concentration in atmospheric carbon dioxide was more than twice as high than in the uncontaminated atmosphere. Local changes of radiocarbon level have also been noted around some nuclear installations. Southern Poland, and particularly the highly industralised Upper Silesia, has numerous coal mines and associated metallurgic, chemical and heavy

industries. Thus it is an area of the biggest changes of radiocarbon concentration in the atmosphere. Radiocarbon measurements in tree-rings from Upper Silesia indicate a significant decrease in ^{14}C concentration compared with "clean air". Changes of the radiocarbon concentration in Upper Silesia in atmospheric CO_2 during the period 1966–1992 can be described by an exponential relation of the form:

$$\Delta^{14}C = 312 \cdot exp(-0.059t)$$

We observed a local decrease of the atmospheric radiocarbon concentration during the growing season in our climatic area. The effect can be described by the parameter: $^{14}S = (-2.3 \pm 1.2)\%$. It is impossible to estimate the total annual effect in samples of plant origin, because the amount of anthropogenic CO_2, which is injected into the atmosphere in the autumn and winter, is not taken into account.

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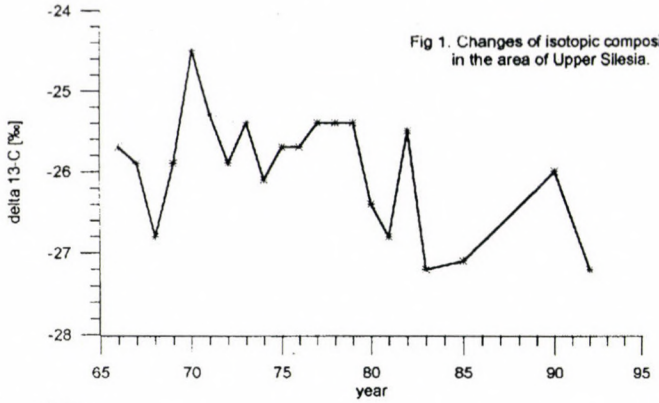

Fig 1. Changes of isotopic composition of crbon in the area of Upper Silesia.

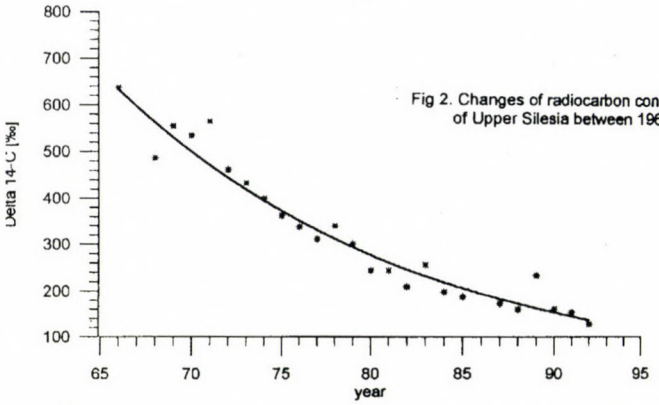

Fig 2. Changes of radiocarbon concentration in the area of Upper Silesia between 1966-1992.

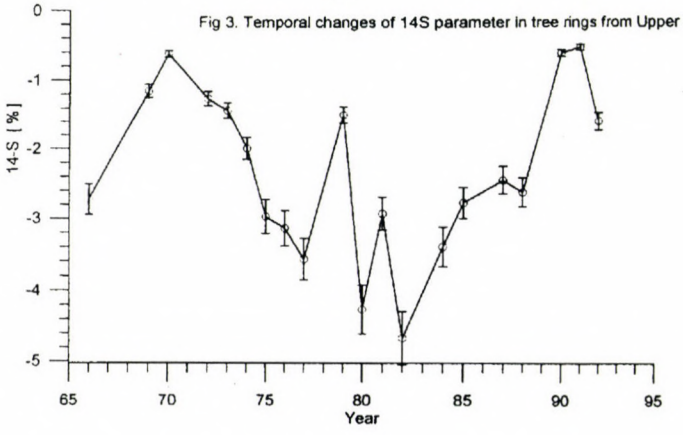

Fig 3. Temporal changes of 14S parameter in tree rings from Upper Silesia.

Fluctuations of $\delta^{18}O$ and $\delta^{2}H$ of the global ocean during Quaternary

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Keywords: oxygen-18, deuterium, stable isotopes, ocean water, Quaternary

The marine oxygen isotope record preserved in deep sea cores represent a history of changing temperature and changing oxygen isotopic composition of the ocean. The isotopic composition of sea water (both $\delta^{18}O$ and $\delta^{2}H$) is directly related to the amount of ice stored in the cryosphere. There were several attempts in the past to separate the temperature and the ice volume component from the marine oxygen isotope records using different approaches: (i) mass balance calculations (e.g. Shackleton, 1967; Dansgaard and Tauber, 1969), (ii) "direct" measurements of ice volume component through oxygen isotope analyses of benthic foraminifera at sites where past temperature changes are assumed to be minimal (e.g. Emiliani, 1958; Savin and Stehi, 1974), (iii) isotopic paleotemperature corrections based on paleontologic data applied to regional oxygen isotope records of benthic foraminifera (Imbrie et al., 1973; van Donk, 1976), (iv) direct calibration of changes in $\delta^{18}O$ of the ocean and the corresponding changes of the sea level, based on isotope analyses of corals (Fairbanks and Matthews, 1978), (v) determination of the temperature component of benthic foraminifera oxygen isotope records using Mg/Ca ratio measured in coexisting ostracodes (Dwyer et al., 1995). The range of estimated changes of $\delta^{18}O$ of the global ocean during the last glacial/interglacial cycle using these different approaches appears to be rather broad: from around $0.6^{o}/_{oo}$ to about $1.6^{o}/_{oo}$. Here, an attempt is presented to assess *both* $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$ using isotope and mass balance calculations for the global ocean. This approach does not require *a priori* knowledge of the mean isotopic composition of the cryosphere in the past.

From the Quaternary perspective the global ocean can be viewed as a huge terminal lake fluctuating around its steady-state value. The present-day total volume of the oceans is estimated to be around 1340×10^{6} km^3 (Leopold, 1974; Baumgartner and Reichel, 1975). The volume of ice caps and continental glaciers is around 28×10^{6} km^3 (Baumgartner and Reichel, 1975). The sea level change between the Last Glacial Maximum (LGM) and the Holocene was about 120 m (Fairbanks, 1989). This corresponds to an addtitional water volume of about 41×10^{6} km^3, stored in ice caps and continental glaciers during the LGM (about 1.5 times the present-day volume). Thus, the relative changes of the "global terminal lake" with respect to its present-day volume were about -3.1% (LGM) and +2.1% (ice caps melted completely). These changes represent the upper limit of fluctuations of the volume of the global ocean throughout the Quaternary. The following mass and isotope balance equations can be formulated for the global ocean:

$$dV/dt = I - E \qquad (1)$$

$$d(\delta_L V)/dt = \delta_I I - \delta_E E \qquad (2)$$

where V and δ_L stands for the volume and the isotopic composition of the global ocean whereas δ_E, E, δ_I, I represent the isotopic composition and the flux of evaporation and total inflow, respectively. The total inflow consists of precipitation over the ocean and continental runoff. For the periods of relatively stable climate (e.g. Holocene) the global ocean should be close to both mass and isotope steady state. Consequently, for these periods the ratio of evaporation to inflow $X = E/I$ is equal one and $\delta_E = \delta_I$. This means that isotopic composition of the net evaporation flux from the ocean is equal to the isotopic composition of the total inflow.

The isotopic composition of the total inflow can be estimated from the database of the IAEA/WMO Global Network "Isotopes in Precipitation" (Rozanski et al., 1993). The estimated global weighted mean isotopic composition of the total inflow ($\delta^{18}O = -5.13‰$, $\delta^{2}H = -30.7‰$) lies very close to the Global Meteoric Water Line: $\delta 2H = 8 \cdot \delta^{18}O + 10$. The line connecting the isotopic composition of the total inflow and the present-day steady-state isotopic composition of the global ocean has the slope equal to 6. This line can be considered a global evaporation line of the ocean.

During the transition periods (glacial/interglacial) the evaporation flux from the ocean is not exactly balanced by the total inflow. Build-up of the ice caps is characterized by $X > 1$ (reduced inflow due to the fact that part of the water is "frozen" in the growing ice caps). Correspondingly, the periods of ice melting will be characterized by $X < 1$. Since the fluctuations of the volume and the isotopic composition of the global ocean are relatively small, with some simplyfiyng assumptions, both $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$ can be derived from eqs.1 and 2. The estimated changes of $\delta^{18}O$ and $\delta^{2}H$ of the global ocean during Quaternary using the above outlined approach are summarized below:

	$\delta^{2}H$ [‰]	$\delta^{18}O$ [‰]	d-excess [‰]
Present-day ocean:	0.0	0.0	10.0
Last Glacial Maximum (LGM):	+9.5	+1.6	6.7
Ice caps melted completely:	-5.5	-0.8	11.5

It should be noted that fluctuations of $\delta^{18}O$ and $\delta^{2}H$ of the global ocean during Quaternary imply changes of the Global Meteoric Water Line. The expected shifts of the intercept (-3.3 ‰ for LGM and +1.5 ‰ for completely melted ice caps), they should be taken into account when interpreting isotope records of ancient precipitation preserved in in ice cores and old ground-waters.

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CARBON AND OXYGEN ISOTOPES IN NEOPROTEROZOIC LIMESTONES: THE BAMBUÍ GROUP - CENTRAL BRAZIL

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key words: Central Brazil, oxygen isotopes, carbon isotopes, Neoproterozoic, limestones

INTRODUCTION

The Neoproterozoic is marked by a global scale occurrence of thick epicontinental carbonate-siliciclastic sequences and glaciation events. Chemical and isotopic variations in these sequences have been used to address stratigraphic problems as well as the environmental conditions during that time. Carbon isotope studies particularly have indicated significant variations in the organic and inorganic carbon reservoirs during the Neoproterozoic (Knoll et al. 1986, Magarizt et al. 1986). These variations control the oxygen level of the atmosphere and may affect, among other processes, the sulfide-sulfate balance of the oceans and the erosion rate of the continents (Veizer et. al 1980). Because of the lack of fossil record and other stratigraphic markers in these sequences, carbon and oxygen isotopes have been used as chronostratigraphic tool within a basin or at a larger scale (Kaufman et al. 1993).

The Bambuí Group constitutes one of the most important Neoproterozoic sedimentary unit in Central Brazil (Fig. 1). This unit occurs over an area of more than 300,000 km^2 and, besides calcitic and dolomitic limestones, it includes sandstones, siltstones, conglomerates, and glacial diamictites (Dardenne 1978). Figure 2 presents a stratigraphic column of the Group and indicates the stratigraphic position of the carbonate sequence studied. The whole sequence was deposited in an epicontinental sea which evolved from carbonate-pelitic domains (Sete Lagoas, Serra de Santa Helena and Lagoa do Jacaré formations) into an essentially siliciclastic domains (Serra da Saudade and Três Marias Formations).

To better understand the environmental conditions during the deposition of the Bambuí limestones, and improve chronostratigraphic unit correlation within the Bambuí basin, an area have been selected to perform a detailed study of oxygen and carbon isotopes. The area is located in the Serra de São Domingos (**SSD**) region and presents one of the best expositions of Bambuí limestones, allowing a systematic sampling of the whole sedimentary sequence (Fig. 1).

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SAMPLING AND ANALYTICAL METHODS

The samples from **SSD** are fresh carbonate rocks sampled along a stratigraphic section of approximately 900 m, which is schematically presented in Fig. 2. Most samples were collected at a regular interval of approximately 10 to 50 m and include both calcitic and dolomitic carbonates, as identified by XRD. Calcite and dolomite comprise more than 80% of the modal composition of the samples.

Carbon and oxygen isotopes were analyzed by reacting samples with 100% H_3PO_4 following McCrea (1950). The released CO_2 was purified cryogenically and analyzed for oxygen and carbon isotopes in a VG Isotech - SIRA II mass spectrometer, at the Stable Isotope Laboratory (LABISE), Federal University of Pernambuco, Brazil.

RESULTS

Figure 2 presents the oxygen and carbon isotopic composition of the samples, arranged according to their stratigraphic position. The isotopic composition of the samples from **SSD** shows a shift of more than 5 ‰, both in $\delta^{18}O$ and $\delta^{13}C$, at the transition between the Sete Lagoas and Lagoa do Jacaré Formations (Fig. 2).

DISCUSSION AND CONCLUSIONS

High values of $\delta^{13}C$ in Neoproterozoic carbonates have been reported in different areas of the globe and have been interpreted due to anomalous organic carbon reservoir increase relative to the inorganic one (Knoll et al. 1986, Margaritz et al. 1986, Kaufman et al. 1995). This increase may have occurred by an increase of the organic production or a decrease of the organic carbon erosion rate. In both cases, large shifts in $\delta^{13}C$ indicate significant changes in environmental conditions.

The data presented here show $\delta^{13}C$ values of up to 10.6‰ (PDB), which may be correlated in a global scale with the high $\delta^{13}C$ values reported by Kaufman et al. (1995) and Magaritz et al. (1986). Although other authors have already reported high $\delta^{13}C$ values for Bambuí limestone (e.g., Iyer et al. 1995, Chang et al. 1993), there is no detailed systematic study along a complete limestone section. In general, our data indicate that most Bambuí limestones have $\delta^{13}C$ values higher than present-day limestones. Data from **SSD** also show a large shift to higher $\delta^{13}C$ values (approximately 6‰), suggesting a remarkable environmental difference between the domains of the intermediate (=+0.8 to +4.1‰) and high (= +6.9 to +10.6‰) $\delta^{13}C$ values (Fig. 2). This shift reflects probably an increase of the organic carbon reservoir towards the top of the section. The $\delta^{18}O$ values also follow the major

$\delta^{13}C$ variations, in spite of the fact that many samples represent mixture of calcite and dolomite, besides other oxygen-bearing minerals. The occurrence of high $\delta^{13}C$ values in other areas of the Bambuí Group indicates that variations of carbon isotopes may constitute an important stratigraphic marker for correlation purposes.

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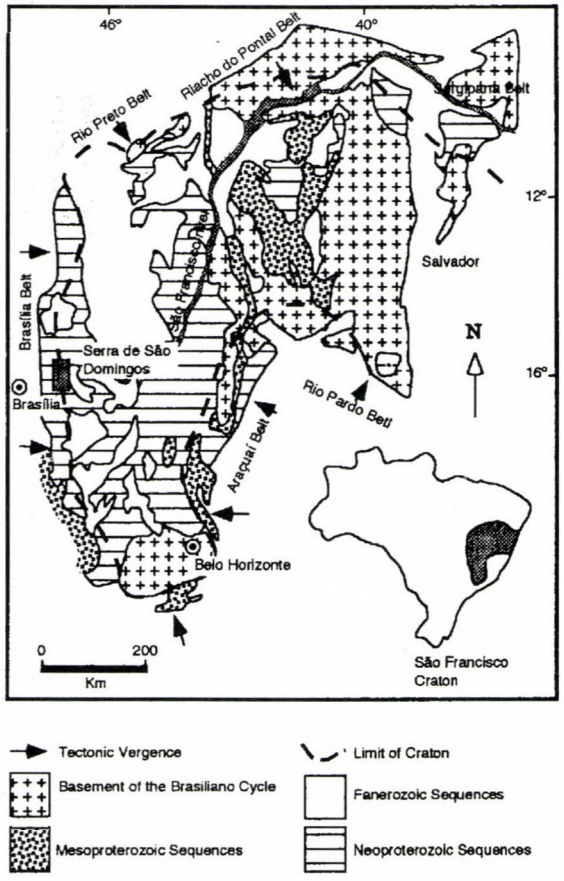

Fig. 1: Geological map of Central Brazil showing the distribution of Neoproterozoic rocks. Adapted from Almeida (1977).

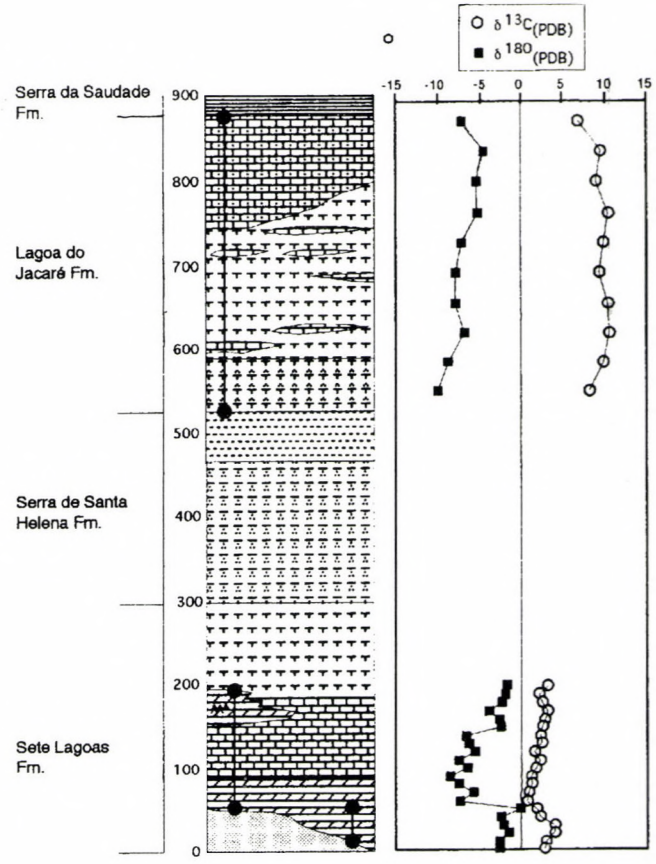

Fig. 2: Stratigraphic column of Serra de São Domingos region. The diagram on the right shows the $\delta^{13}C$ and $\delta^{18}O$ data of this work.

O, H, S AND Sr ISOTOPES IN TWO BRASILIANO-AGE GRANITIC INTRUSIONS, STATE OF CEARA, NE BRAZIL

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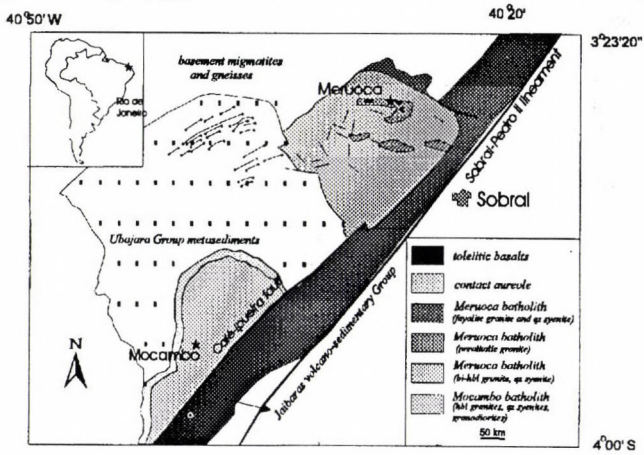
Keywords: granite, epizonal, peralkalic, O isotopes, Sr isotopes, NE Brazil, Brasiliano orogeny

INTRODUCTION: The Meruoca and nearby Mocambo unfoliated, post- kinematic epizonal plutons 240 km west of Fortaleza are two of the few granitoids in the state that have been studied in detail. The plutons are located near the western marginal fault of a graben (Fig. 1) whose sedimentary filling probably correlates with the Buem Series in Ghana and Togo, west Africa.

Granite-roof facies are still preserved in the 400 km^2 Meruoca batholith. It consists of granite, quartz syenite, and alkali-feldspar granite of a dominant gray, or brick-red fayalite-free facies, gradational into a gray, green, or brown fayalite-bearing facies in its northern part. The fayalite-free facies (including pegmatitic to very fine-grained aegirine and/or riebeckite-bearing rocks in the central and eastern portions) contain abundant graphic and granophyric intergrowths and drusy miarolitic cavities. These epizonal textures are less common in the fayalite-bearing rocks which are slightly porphyritic with feldspar phenocrysts averaging around 2 cm. Presence of turbid brick-red feldspar over large areas indicates that the high-level Meruoca pluton experienced pervasive, hydrothermal alteration. Crystallization occurring mostly under reducing conditions (except where aegirine is present) resulted in Fe-rich biotite and scarce magnetite. Log of f_{H2O} is estimated to have been 3.5 from biotite chemistry.



The 180 km^2 Mocambo pluton to the south, is comprised of porphyritic granodiorite to quartz monzonite to quartz syenite, and hornblende-biotite granite. In this pluton, granophyric intergrowths and miarolitic cavities are uncommon. At Mocambo, magmas crystallized mostly at low oxygen fugacity.

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Contribution n. 84 of the Nucleus for Granite Studies(NEG) and n. 16 of the LABISE, UFPE, Brazil

The metasedimentary Ubajara Group, host to both plutons, is weakly metamorphosed, into which are emplaced numerous ENE-trending diorite and latite to rhyolite dikes that in turn are cross-cut by the Meruoca granite. Where not bounded by faults, both plutons intrude the host metasediments discordantly, and Mocambo has a well-developed contact aureole whose mineralogy indicates shallow emplacement.

MAJOR AND REE CHEMISTRY

At Meruoca, both the fayalite-bearing and fayalite-free facies are classified as (i) peralkalic, alumina-depleted, and Fe^{+3}-enriched, or (ii) subalkalic, alumina-enriched, with lower Fe_2O_3. Both groups have similar K_2O (up to 6%), and lower Na_2O (~ 3 %). Trends in a Mg-Zr plot show gentle slope (subalkalic facies) or a steeper slope (peralkalic facies).

Chemical trends suggest that quartz syenite formed by preferential Kspar fractionation from the parental magma, leading to residual peralkalic magma that crystallized at a higher oxidation state. MORB-normalized elemental concentration diagrams for fayalite-bearing and fayalite-free rocks show LILE-enriched patterns with a negative slope, and pronounced P and Ti troughs.

The Mocambo pluton pluton exhibits a dominating intermediate-K and a subordinate high-K trend, and K_2O/Na_2O ratio similar to that observed in Meruoca rocks.

REE patterns for the two intrusions are similar, exhibitting smooth-trending LREE and a prominent negative Eu anomaly. Concentrations of total REE are very high (up to 1600 ppm).

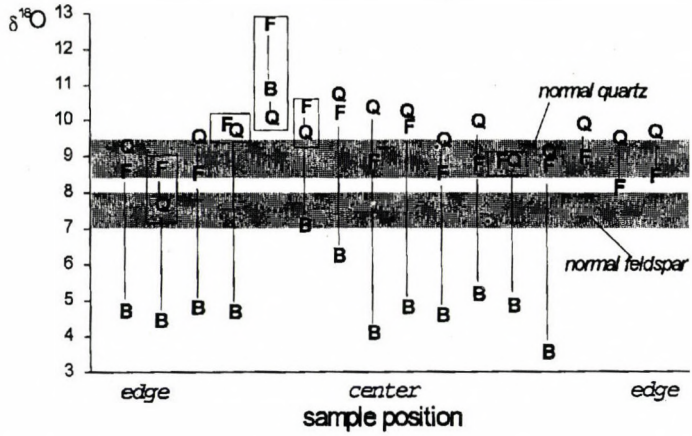
Sample data from Mocambo form a linear trend parallel to, and near to the subalkalic trend of Marejuol et al. (1987) in the R_1-R_2 diagram. With two exceptions, data plot near the syncollisional domain in this diagram. In contrast, data from subalkalic and peralkalic rocks of Meruoca form a continuous trend, the latter with lower R_1 values than the former, approaching the postorogenic domain.

STABLE ISOTOPE GEOCHEMISTRY

We have nearly 150 analyses of $\delta^{18}O$ for Meruoca whole rock and separted quartz, feldspar, biotite, and hornblende, and Mocambo whole rock, and 22 δD analyses of whole rock and separated biotite (annite) and three whole-rock $\delta^{34}S$ data from Meruoca and Mocambo.

(a) Oxygen isotopes: In Meruoca, whole-rock quartz, feldspar, or biotite $\delta^{18}O$ values form a a remarkable bull's eye pattern centered somewhat asymmetrically about a location where the pluton is penetrated by basalt dikes and associated flows. Toward the periphery the pluton appears to be normal I-type granite ($\delta^{18}O$ = +7 to +8‰$_{SMOW}$), but in the bull's eye all the minerals including quartz are exceptionally heavy ($\delta^{18}O_{spar}$ approaching +13‰). Several quartz-feldspar pairs are in isotopic disequilibrium (Fig. 2). Two superimposed phenomena may have contributed to the stable isotope pattern. The highest $\delta^{18}O$ occurs where the granite roof (containing riebeckite) is preserved, where it once lay adjacent to high-$\delta^{18}O$ host rock (+13 to +14‰). Brick-red feldspar and $\delta^{18}O$ disequilibrium (quartz-feldspar) indicate a prolonged, late, low-temperature interaction with meteoric water.

Five whole-rock $\delta^{18}O$ values for Mocambo range from +9 to +10‰, predominating values close to +9.0‰. Such homogeneity suggests that these values are primary or that if any post-magmatic modification took place, it did not change them drastically. These values are close to the upper limit for I-type granites according to O'Neil et al. (1977).



Values of $\delta^{18}O$ in the dikes to the west of the Meruoca pluton range from +9.5 (latite), to +11‰ (rhyodacite). Correlation of whole-rock $\delta^{18}O$ with SiO_2 suggests that the observed 1.5‰ variation reflects the weighted abundance of mafic minerals (light), feldspar (intermediate), and quartz (heavy). There is a gradual systematic increase in $\delta^{18}O$ values from the southernmost to the northernmost dike which correlates with their petrographic variation from south to north (latite-dacite-rhyodacite-rhyolite). This might indicate that the dikes are cogenetic and subsequently intruded from the southernmost to the northernmost one.

(b) **Hydrogen isotopes**: Thirteen whole-rock δD analyses (Meruoca) vary from -52 to -89‰ (average -75‰) and 9 biotite analyses are -76 to -92‰ (average -85‰) consistent with uniform Mg/Fe ratios that are also within the "normal" range for igneous rocks. There is no positive correlation between δD and F/H_2 in whole rock or biotite (fluorine did not play an important role in H isotope fractionation). If whole-rock δD=-80‰ suggests I-type and δD= -60‰ suggests S-type (O'Neil et al. (op. cit.)), then the source for Meruoca is predominnatly I-type.

(c) **Sulfur isotopes**: Values of whole-rock $\delta^{34}S$ of 2.9 to 3.1‰ resemble those for I-type granites in the Lachlan Foldbelt (Coleman, 1979) or magnetite-series granitoids in Japan (Sasaki & Ishihara, 1979).

Rb-Sr ISOTOPE SYSTEMATICS

A whole-rock Rb-Sr isochron (14 samples) provides an age of 491 ± 19 Ma and R_i= 0.7076 ± 0.0028, but with data scattering well outside experimental error attesting to a significant disturbance of the Rb-Sr relatiosnhips. Data for samples with the lowest Sr plot well off the main isochron trend, and are indicated to be in oxygen isotope disequilibrium.

A whole-rock Rb-Sr isochron for Mocambo yields an emplacement age of 544 ± 15 Ma and an initial ratio of 0.7106 ± 0.0008 for the batholith.

CONCLUSIONS

The epizonally emplaced Meruoca batholith illustrates the mutual correspondence of anomalous O and Sr isotope data patterns. A similar pattern is found in the St. François Mountains, Missouri, USA (Wenner & Taylor, 1976), where there is also a systematic increase $\delta^{18}O$ towards the center of a pluton. The oxygen isotope study of the dikes to the west of the Meruoca batholith also proved to be a useful tool in determining the probable order of dike emplacement.

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Stable oxygen isotopes in mammal bones from archaeological sites in Middle and West Europe reflecting climate changes during the Last Glacial and the Holocene

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Keywords: stable oxygen isotopes, animal bones, archaeology, climate, Pleistocene, Holocene, Europe

Introduction

The influence of climate on morphologic and isotopic features of bones from large mammals during the last 500.000 years in Middle Europe is investigated as part of a special research project (SFB 275) at the University of Tübingen. Little is known about correlations between changes in climate and possible effects on the isotope ratios of animal bones. Initial, work is limited to two species: reindeer, *Rangifer tarandus*, and horse, *Equus sp.*, which are found regularly in Pleistocene deposits and for which the biology is well known. After the osteometrical analysis of the bone samples the $\delta^{18}O$ in the hydroxyapatite is measured. We expect, that shifts on the isotope ratios are directly related to changes in climate. In archaeology, climatic statements are usually given by the species distribution, pollen, macrobotanical, and sedimentoglogical analyses and dated occurrences. Often such considerations are limited to the occurrence of certain spcies. But this does not include the large range of climatic adaptation of many major species.

Stable oxygen isotopes in animal bones

The oxygen isotope ratios in animal bone tissue are part of the global oxygen cycle. The oxygen isotope ratios in the drinking water change largely as a function of temperature, humidity, and other related effects. Caused by different habits species have an uptake of drinking water with different oxygen isotope ratios. During uptake in the body, the isotope ratios are changed by fractionations which are independent of the environmental temperature but characteristic for certain species. The fractionations continue (at a body temperature of 37°C) until the oxygen isotopes are incorporated in the hydroxyapatite of the bones. Investigations of recent living animals showed that the $\delta^{18}O$ values of meteoric water are positively correlated with the $\delta^{18}O$ of the body fluids, and the $\delta^{18}O$ of the bone phosphate (Longinelli, 1984; Luz & Kolodny, 1985). Because of this linear relationship between the oxygen isotope ratios of drinking water and bone phosphate and because of the diagenetic stability of phosphate, the $\delta^{18}O$ values of animal bones reflect the temperature of the drinking water at the time of formation of the hydroxyapatite. It is, therefore, possible to draw conclusions about palaeoenvironments on the basis of the oxygen isotope ratios of bone phosphate (Ayliffe and Chivas, 1990; Luz et al., 1984; Luz, et al., 1990).

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Material

Bones from cattle raised in the vicinity of Tübingen were used to establish the preparation and measurement techniques (Tab. 1). Cattle and musk ox bone samples, taken from Holocene archaeological sites situated in different climate regions of the earth (Tab. 1), were measured to estimate the relation of oxygen isotopes in terrestrial mammals to climate. Pleistocene samples were recovered from different archaeological sites in Germany. Investigated species are *Equus sp.* and *Rangifer tarandus* . The sites are dated to the end of the last glaciation (Wurm glacial) (Fig. 2)

Experimental methods

After mechanical cleaning and washing of the whole bone sample, about 1g was taken from the diaphysis and pulverized to <0,125mm for isotopic analysis. Oxygen isotope analysis followed a modified version of the method described by O´Neil et al. (1994). The modifications include the removal of humic substances and lipids using diluted solutions of sodium hydroxide and sodium hypochlorite. The isotope ratios were measured with a Finnigan MAT 272 mass spectrometer and are reported relative to VSMOW.

When sufficient samples are available from one site, several individuals were analyzed to obtain representative analysis from populations rather than from individual samples.

Analytical results and discussion

The results in Tab. 1 and Fig. 1 (Stephan, in press) show a clear correlation between the oxygen isotope ratios of the Holocene bone samples and the climate zones. As expected, higher average temperatures correspond to higher $\delta^{18}O$ values of the bone samples. Musk ox bones from Umingmak/Arctic Canada have very low $\delta^{18}O$ values whereas the $\delta^{18}O$ values of cattle bones from the United Arab Emirates are about 25‰ higher. For sample populations within individual zones, cooling could be observed during the settlement periods of Tell Abraq from 2000 B.C. to the 1st half of the 1st millennium B.C. (Subboreal period). A simliar trend exists for the Troy bone samples over 3000 years from 3000 B.C. onwards.

As for the Holocene and recent data, the results of Pleistocene samples in Fig. 2 show a positive correlation between climate and $\delta^{18}O$ values and vice versa between cooling periods and lower $\delta^{18}O$ values. The reindeer bones of the sites in northern Germany also had much higher $\delta^{18}O$ values during the warming period at the end of the Wurm glacial, Bølling (sites No. 2 and 3), compared to the end of the last cooling phase, the Younger Dryas (site No. 1), and to the cooler Older Dryas (Equus bones from Andernach, site No. 4). The Equus bone samples from sites in southern Germany sites have lower $\delta^{18}O$ values compared to those of northern Germany. Two reasons account for this difference: 1) lower $\delta^{18}O$ values of meteoric water in the more continental part of southern Germany (site No. 5 and 6) and 2) the age of the site (No. 6), where samples are from the end of the Oldest Dryas.

Conclusions

Oxygen isotope ratios of bone phosphate from grazing mammals appear to provide a good basis to reconstruct past climates. Future work will concentrate on well dated Pleistocene sites in Middle Europe. Initial work started at the end of the Wurm glacial. While future work will move backwards in time.

Table I: Results of recent and archaeological animal bones from different climate zones

Site Dating	Region	Climate zone Temperature	Species	$\delta^{18}O$ ‰ vs. VSMOW
Umingmak ^{14}C:1500 B.C.	Banks Island/ Arktic Canada Coastal Site	arctic, tundra zone; dry winter: -40 to -30°C summer (short): -0 to +10°C	*Ovibos moschatus*	6,21
Tübingen recent	SW-Germany Inland Site	warm, temperate zone; humid	*Bos taurus*	13,82
Heuneburg 6th. Cent. B.C.	SW-Germany Inland Site	winter: -10 to 0°C summer: +10 to +20°C	*Bos taurus*	15,27
Troy 3000-2800 B.C. 2500-1500 B.C. 500 B.C. - 500 A.D.	NW-Turkey Coastal Site	mediterranean, subtropical zone humid winter, dry summer winter: 0 to +10°C summer: +20 to +30°C	*Bos taurus*	18,64 18,16 17,37
Tell Abraq 2000 B.C. 2000-1300 B.C. 1000-600 B.C.	United Arab Emirates Coastal Site	arid, tropical zone; in summer arid in winter (3 month) humid winter: +20 bis +30°C summer: +30 bis +40°C	*Bos taurus*	28,21 24,28 22,84

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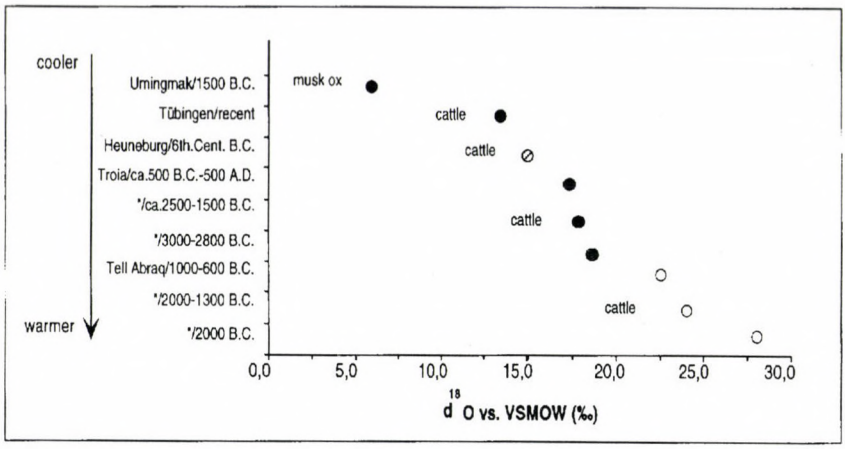

Fig. 1. Oxygen isotope ratios in herbivore bones from archaeological sites in different climate zones

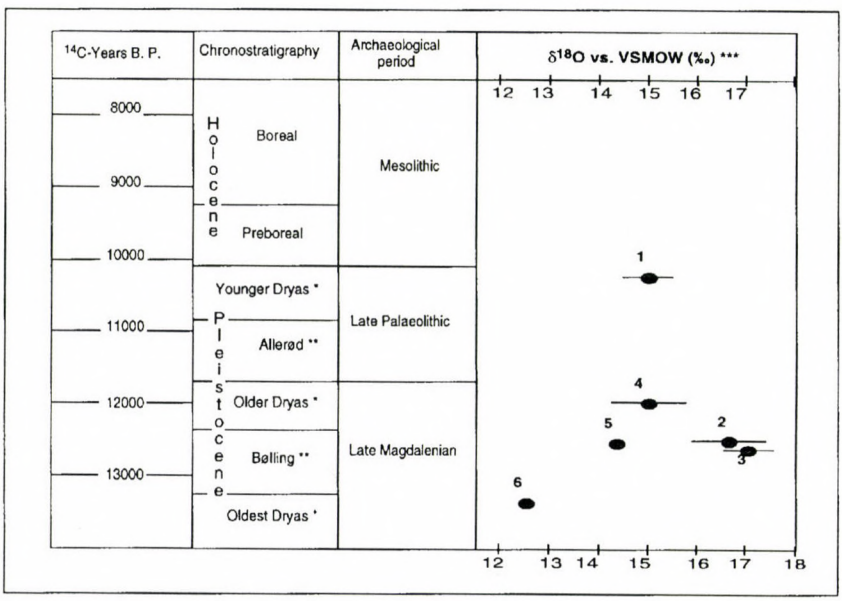

Fig. 2. Chronology, chronostratigraphy, archaeological period, and $\delta^{18}O$ values of reindeer and horse bones from archaeolgcial sites in Germany.

* period of cooling; ** period of warming; *** arithmetical mean and standard deviation (1σ)
Species/Site/Culture/Region:
1 Rangifer tarandus/Stellmoor/Ahrensburger Kultur/Northern Germany (N=10)
2 Rangifer tarandus/Stellmoor/Hamburger Kultur/Northern Germany (N=10)
3 Rangifer tarandus//Meiendorf/Hamburger Kultur/Northern Germany (N=10)
4 Equus/Andernach/Western Germany (N=10)
5 Equus/Hohlenstein-Stadel/Southwest Germany (N=1)
6 Equus/Spitzbubenhöhle/Southwest Germany (N=1)

Deep aquifer systems in the South-West German Molasse Basin

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GLA Baden-Wuerttemberg, Freiburg

The whole area under investigation is the South German Alpine foreland, between the Alps and the Danube valley. There are mainly two aquifers: the upper aquifer in the Tertiary Upper Marine Molasse (German code:OMM) and the lower aquifer in the karstified Malm. They are separated from each other by thick sequences of the Lower Freshwater Molasse (USM) which show low permeability of about 10^{-9} to 10^{-11} m/s in most areas. The OMM is widely covered by deposits of the Upper Freshwater Molasse (OSM) also of rather low permeability. Most data, both from hydrogeology and from the Quaternary, are available from Oberschwaben, the South-West part of the Molasse Basin.

This part of the research area is used for hydrogeothermal purposes. The management of these hydrogeothermal resources requires good knowledge of the general flow systems, the available groundwater amount and the geothermal conditions. Therefore this South-West part of the basin was intensively investigated since about 20 years. Besides extensive hydrochemical investigations, many measurements of environmental isotopes were carried out. In this presentation the results of ^{2}H, ^{3}H, ^{13}C, ^{14}C, ^{18}O, ^{34}S and noble gas analyses are presented. The correlations of ^{18}O to ^{14}C and ^{18}O to temperature deduced from noble gas measurements are given in Fig. 1 and 2 as examples.

These geohydraulic, hydrochemical and isotope-hydrological investigations indicate two flow systems in the Malm aquifer. The part of the Malm aquifer at the northern border of the research area contains groundwater of a Ca-Mg-HCO_3 - Type. This groundwater shows higher ^{2}H- and ^{18}O contents and temperatures, deduced from noble gas measurements, which indicate climatic conditions during recharge like in the Holocene. The part of the Malm aquifer more in the center of the basin shows groundwater of a Na-Ca-HCO_3-Cl - Type. The stable isotope contents (^{2}H and ^{18}O) are lower and the temperatures, again calculated from the noble gas analyses, indicate pleistocene climatic conditions during recharge. Also different recharge mechanisms exist in both systems and were discussed.

The proportion of pleistocene paleo-groundwater and recently recharged groundwater is mainly responsible for the geothermal management. Hydrochemical and isotope-hydrological investigations gave better insight into the complexity of the recharge mechanisms. Possible consequences will be discussed for the use of these geothermal groundwater in the future.

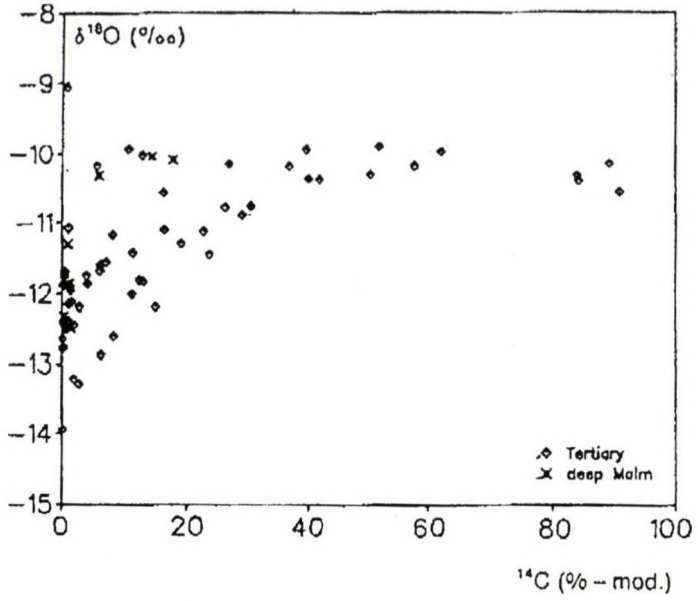

Fig. 1: Relation between ^{18}O content and ^{14}C values of groundwater from Tertiary and Malm karst aquifer.

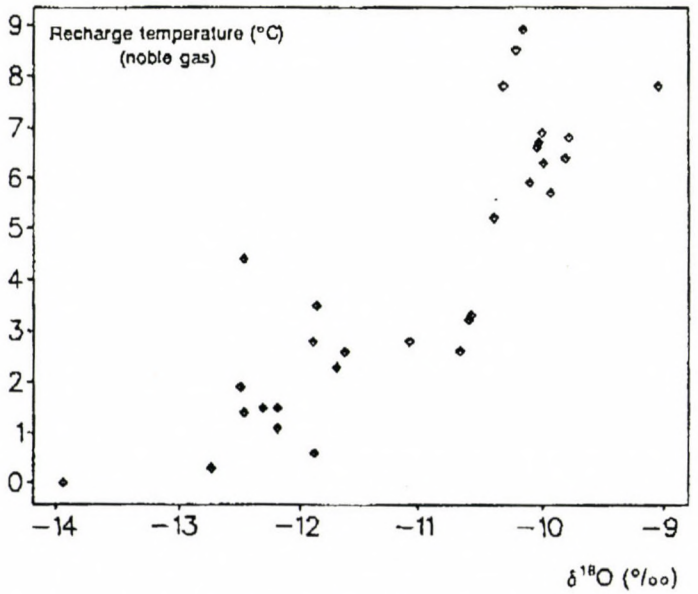

Fig. 2: Relation between ^{18}O content and temperature deduced from noble gas measurements from Tertiary and Malm karst aquifer.

Acid Fractionations of ^{18}O and ^{13}C in CO_2 Preparation from Dolomite – Calcite Mixture

Janina Szaran[1] and Halina Niezgoda[1]

Keywords : $\delta^{18}O$, $\delta^{13}C$, calcite, dolomite, acid fractionation

In geological studies of dolomites frequently the dolomite samples contain impurities of calcite which result in some difficulties of isotopic analysis of dolomites. It is the purpose of this study to use difference in CO_2 production rate by phosphoric acid to infere optimum preparation conditions of impure dolomites.The experiment was performed on three samples of natural dolomite with an admixture of calcite of 14.9%; 10.3% and 4.7%, respectively.

Defined quantities (20 - 40 mg) of the tiny pulvered sample were put into one arm of the reactor the volume of which was 125 cm^3. About 5 cm^3 of 100% H_3PO_4 was poured into the second arm of the reactor. The apparatus was evacuated and subsequently the sample was treated with the phosphoric acid at temp. 25°C. After some time of the reaction (from 10 minutes to 2 hours) the first fraction of CO_2 was extracted cryogenically and transferred into a small ampoule. The reactor was then kept at temperature 50°C to accelerate the reaction of H_3PO_4 with dolomite. When the reaction was completed, CO_2 was collected in a separate ampoule as the second fraction.

The collected fractions of CO_2 were analysed mass-spectrometrically, using a triple collector system (Durakiewicz and Hałas 1994). The relative amounts of CO_2 in both fractions and their $\delta^{13}C$ and $\delta^{18}O$ were determined. The determination of the amount of CO_2 was performed by recording the major beams in CO_2 spectra for the boths fractions admitted to the inlet system at its minimum volume. $\delta^{13}C$ and $\delta^{18}O$ values of each fraction as a function of the reaction time for the first fraction are summarized in Table I and plotted in Figures 1 and 2, respectively.

It is clearly visible that the first fraction of CO_2 (dashed line in Figure) is depleted with respect to the second in heavy isotopes of oxygen (up to $4‰$) as well as of carbon (up to $6‰$). The largest depletion is for the shortest reaction time. The carbon and oxygen isotopic composition of the second fraction is nearly constant or shows a very small dependence upon reaction time for the first fraction. We can assume that the first fraction of CO_2 is produced from calcite which normally reacts at 25°C (McCrea 1950), whilst the second comes predominantly from dolomite. To verify this assumption we will continue the experiment but with pure calcite, pure dolomite and their defined mixture.

We thank professor S. Hałas for suggestion of this study and for comments on the manuscript.

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Table I. Values of $\delta^{13}C$ and $\delta^{18}O$ in the first and in the second CO_2 fraction for different reaction times.

Sample	Reaction time for I fraction [min]	CO_2			
		I Fraction		II Fraction	
		$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
No 1 14.9% calcite	10	-4.50	-5.88	1.43	-2.19
	20	-3.16	-5.56	1.38	-2.02
	30	-2.78	-4.99	1.46	-2.16
	60	-1.57	-4.41	1.63	-2.00
	90	-1.19	-3.94	1.71	-2.24
	120	-0.85	-2.74	1.94	-2.09
No 2 10.3% calcite	10	-5.83	-6.93	0.33	-3.26
	30	-4.06	-5.53	0.73	-2.91
	60	----	-4.91	0.51	-2.61
	90	-2.45	-4.37	0.62	-3.17
	120	-2.28	-4.25	0.53	-2.39
No 3 4.7% calcite	10	-5.24	-5.82	-1.85	-2.28
	20	-4.20	-5.13	-1.88	-2.57
	35	-3.65	-3.84	-1.87	-2.48
	75	-3.06	-3.72	-1.84	-2.74
	120	-2.77	-2.61	-1.85	-3.25

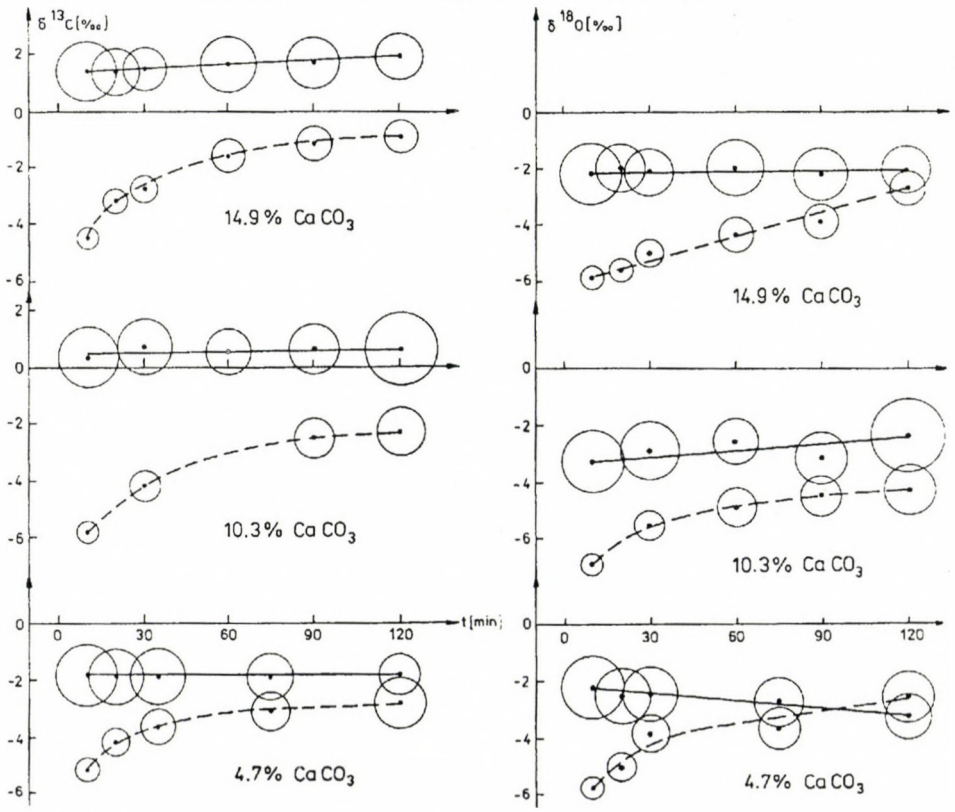

Fig. 1 $\delta^{13}C$ plot for the two fractions as a function of the reaction time for the first fraction. The first fraction is presented by dashed line. Circle surface is proportional to the amount of CO_2.

Fig. 2 Same as Fig. 1, but for $\delta^{18}O$.

Analyses of $\delta^{13}C$-ratios from inorganic and organic carbon in clay liners for waste disposals

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keywords: stable carbon isotopes, analytical methods, waste disposal, clay barrier, carbonate, inorganic carbon, organic material.

Introduction

Barrier systems in modern waste disposals include clay liners, which are designed to protect the environment from aggressive and toxic leachates. They must a) have a very low hydraulic conductivity and b) have a high capacity to adsorb pollutants such as heavy metals and organic compounds. Since they are responsible for long-time security of a waste disposal site, they must retain this quality over longer periods of time.

Natural clay liners also contain carbonates as well as organic materials. However, interaction of aggressive leachates with these phases will result in geochemical and mineralogical changes and thus influence the quality of the clay liner. As part of a recent reseach project clay-materials were treated with 10% acetic acid 8 to 60 weeks and the behaviour of carbon bearing phases studied, in order to assess their impact on the stability of a clay liner (TAUBALD & SATIR, 1994, TAUBALD, 1995). Dissolution and precipitation processes were evaluated by quantitative analysis and $\delta^{13}C$ values of the carbon bearing phases. A conventional acid extraction method was used for analysis of inorganic carbon in carbonates (McCRAE, 1950) and an elemental analyser combustion method for organic carbon, total carbon as well as inorganic carbon (after organic carbon was removed by roasting in air at 520°C). However, comparison of the two methods showed, that no consistent results could be derived, and problems arose in interpreting the data.

Analytical methods

A carbonate bearing Tertiary clay (about 60% montmorillonite, illite and kaolinite) with about 35% carbonate (28% calcite, 7% dolomite, no aragonite could be observed so far) and 0,2% primary organic material was treated 8, 15, 30 and 60 weeks (see Table I) in permeability cells under laboratory conditions (atmospheric pressure, 25°C) with a 10% solution of acetic acid (pH 2.3, $\delta^{13}C$ = -30‰). About 50g of these samples and an untreated raw material were dried at 110°C and ground to 63µm, of which 25g was roasted at 520°C under atmospheric conditions to remove any organic material (similar to CRAIG, 1953, who removed organic material at 475°C in a helium stream).

In a conventional acid extraction line (after McCRAE, 1950) the analysis of $\delta^{13}C$ was performed on CO_2 generated by reacting 10-500mg powder with 100% H_3PO_4 at 25°C over 7 days (due to 7% dolomite being present). Simultaneously carbonate was measured

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quantitatively by calculating the amount of CO_2 extracted from the carbonates. Acid extracted samples were prepared off-line and sealed in 6mm glas tubes. In an elemental-analyser combustion unit 1-50mg powder was analysed for $\delta^{13}C$ values of total carbon. In an oxygen and helium stream the sample powder was combusted at 1800°C, CO is avoided by oxidation to CO_2 with CuO at 900-1000°C. Quantitative determination of carbon was done by measuring the amount of CO_2. Samples measured with the elemental analyser were prepared on-line, CO_2-gas was purified from oxygen, helium and N_2 by trapping at -196°C with liquid nitrogen. Roasted and unroasted samples as well as untreated raw materials were analysed. The analytical error of $\delta^{13}C$ values is ± 0.1‰, the relative error of quantitative carbonate and carbon determination is 3%. All isotope ratios were measured with a Finnigan MAT 252 and are reported relative to PDB.

Results and discussion

The results are given in Table I. With the acid extraction method only inorganic carbon in carbonates can be measured isotopically on the roasted samples. The results show, that roasting the samples at 520°C removes organic matter but also, unexpectedly, changes the isotopic composition of the carbonates. The raw, untreated material is shifted to more negative values by 0.4‰, while most acid treated samples show changes around 1‰ and samples 15W1 and 30W1 reveal the greatest shifts of 13.9 and 14.3‰. This is correlating with the amount of carbonate dissolved by acetic acid. In contrast pure carbonate shows no difference between roasted and unroasted samples. This is evidence, that a) organic matter is playing a significant role when the carbon isotope compositions of the carbonates are determined according to the McCRAE method or b) that fractionation of carbon isotopes in carbonates occurs during combustion of organic matter at 520°C.

With the elemental analyser inorganic and organic carbon is measured as total carbon. Since the $\delta^{13}C$-value of organic matter in this clay is -25.6‰, the value of -3.5‰ for the raw material can be explained by mixing inorganic (-2.5‰) with primary organic carbon. The results of the acid treated samples show the influence of acetic acid ($\delta^{13}C$ = -30‰). The more carbonate is dissolved, the higher is the influence of organic carbon from acetic acid and from primary organic matter. This can be seen in the amount of total carbon, which is about 0.5 to 1.0 % higher than in untreated material and correlating with the isotope ratios, which are significantly more negative by 3 to 5‰ compared with untreated material. Pure carbonate, measured as a standard, showed that the difference between the two methods is in the range of 0.3‰.

Roasting and removal of organic matter depleted in ^{13}C shifts the isotope ratios to more positive values. When the materials are roasted at 520°C and primary organic carbon as well as organic carbon from the acetic acid is removed, the $\delta^{13}C$-values of the elemental analyser should give the same values as the conventional acid extraction method, since only inorganic carbon should be present. This is true for the roasted samples, apart from 3 samples with very low carbonate content, that still show differences of about 1-2‰, all values lie within the analytical accuracy of 0.3‰ as defined by the pure carbonate standard.

Conclusions

Primary organic carbon as well as organic carbon from acetic acid may have an influence on the $\delta^{13}C$ values of carbonate phases when measured with conventional acid extraction method. This is the reason why CRAIG, 1953 recommended a pretreatment of samples which "contain appreciable organic matter" by roasting at 475°C in a helium stream.

However a helium stream can not provide enough O_2 to oxidise all organic carbon to CO_2 and part of it will remain in the sample as graphite. In this work pretreatment of the samples was performed by roasting at 520°C under atmospheric conditions. The results show, that using this pretreatment the same results are obtained for carbonates analysed by the two distinct methods. However, this does not say anything about what are the "correct values". If there is a direct influence of organic matter depleted in ^{13}C on the $\delta^{13}C$ value of the total powder, the roasted samples should give more positive values. This can be seen when $\delta^{13}C$ values of roasted and unroasted samples measured with the elemental analyser are compared. Roasted samples analysed with the conventional method, however yield more negative values that unroasted ones.

LAND, 1989 showed in a brief summary of analytical procedures that different methods of pretreatment are used to determine isotope ratios of carbonate phases (if its not pure carbonate) and that "organic matter is commonly blamed" for obvious differences in isotopic results. The data presented here prove that organic matter is playing a significant role. However, the facts, that a) roasted samples show more negative $\delta^{13}C$ values with the acid extraction method and b) that only the roasted samples give the same results with different analytical methods, emphasize, that this influence is complex. A possible explanation may be organic matter structurally adsorbed onto clays, that is decomposed and released by H_3PO_4, however further research has to be done.

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Table I: Analytical results, for further explanation see text. All isotope ratios are given relative to the PDB standard. "EA" means measured with cumbustion in elemental analyser, "acid ex." means conventional method by McCRAE, 1950.

Sample	$CaCO_3$ %	total Carbon %	$\delta^{13}C_{acid\ ex.}$	$\delta^{13}C_{EA}$	roasted at 520°C $\delta^{13}C_{acid\ ex.}$	roasted at 520°C $\delta^{13}C_{EA}$
raw, untreated material	35	4.5	-2.5	-3.5	-2.9	-3.0
pure carbonate standard	100	12	-10.5	-10.8	-10.5	-10.8
8W1	3.3	2.1	-2.3	-23.8	-6.7	-6.4
8W2	25.1	4.9	-1.7	-9.0	-3.1	-3.0
8W4	31.2	5.2	-2.2	-7.5	-3.2	-3.4
8W5	30.7	4.8	-2.2	-7.8	-3.4	-3.3
8W6	32.0	5.0	-2.2	-7.3	-3.3	-3.6
8W8	34.1	5.3	-2.5	-7.3	-3.5	-3.5
8W10	32.2	5.0	-2.2	-7.5	-3.0	-3.3
8W12	32.3	5.1	-2.2	-8.7	-3.6	-3.6
15W1	3.0	1.3	+1.7	-28.2	-12.2	-14.1
15W2	20.3	3.4	-0.7	-9.2	-1.8	-2.2
15W4	33.6	5.0	-2.0	-6.4	-2.8	-3.0
15W5	33.0	4.9	-2.3	-6.3	-3.0	-3.0
15W6	30.9	4.7	-2.7	-5.9	-3.0	-3.4
15W8	34.7	4.9	-2.0	-5.6	-2.8	-2.8
15W10	32.9	4.8	-2.0	-6.1	-2.9	-3.0
15W12	34.0	5.0	-2.0	-7.2	-3.1	-3.1
30W1	0.5	3.3	-7.0	-29.9	-21.3	-22.6
30W2	13.0	3.4	-1.2	-15.1	-3.5	-4.0
30W4	31.6	4.9	-2.2	-7.8	-3.2	-3.3
30W5	33.5	5.4	-2.1	-9.2	-3.0	-3.1
30W6	32.1	5.1	-2.2	-8.2	-3.5	-3.3
30W8	33.4	5.1	-2.2	-8.1	-3.3	-3.2
30W10	32.0	4.7	-2.2	-7.4	-3.3	-3.3
30W12	33.6	5.4	-2.1	-8.5	-3.4	-3.3
60W4	4.1	3.3	+1.4	-24.4	-8.8	-9.9
60W5	29.4	5.3	-1.9	-10.3	-3.2	-3.5
60W6	33.1	5.3	-2.2	-8.6	-3.3	-3.4
60W8	33.2	5.2	-2.3	-8.4	-3.3	-3.8
60W10	33.5	5.2	-2.5	-8.2	-3.4	-3.9
60W12	33.8	5.2	-2.3	-7.9	-3.5	-3.5

SOME CONSIDERATIONS ABOUT RADIOCARBON METHOD IN CARBONATE FISSURED AQUIFERS

(Case studied: South Dobrogea, Romania)

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Key words: groundwater, radiocarbon dating, actual velocity, correction methods, South Dobrogea.

I. Introduction.

Radiocarbon has proved to be extremely useful in the hydrogeology of regional aquifers or with low flowing velocity. Relatively close results between ^{14}C and hydraulic methods were obtained in the porous aquifers, especially with a non-carbonate matrix. Major disagreements have however occurred for fissured limestone aquifers where, the application of ^{14}C method has more conditioning but, at the same time, the results of the classical hydrogeological methods are also very relative in these situations. In such cases the radioisotopic ages occur as overestimated and require corrections. This is also the case of fissured-karstified calcareous aquifers in South Dobrogea.

II. Theoretical background.

In the hydrogeological practice and especially in the mathematical modeling of the hydrostructure it is extremely useful to know such parameters as:

- ***water age*** t_w (turnover time), defined as: $t_w = V_m / Q$ (1), where V_m - the volume of the mobile water and **Q** - volumetric flow rate through the system.
- ***actual flow velocity*** **v**, defined as: $v = v_D / n$ (2), where v_D - Darcy's velocity ($v_D = k * I$) and **n** - effective porosity.

Other two necessary concepts are:

♣ *The radioisotope age* t_a , usually included in: $c / c_o = \exp(-\lambda * t_a)$ (3), the equation of radioactive decay, where c_o and **c** are the initial and the measured radioisotope tracer concentrations and λ is the radioactive decay constant. When c_o = 100 pMC, we talk about a radiometric age; but as the initial activity is corrected (c_o < 100 pMC) the results obtained are radioisotopic ages.

♣ *The tracer velocity* v_a , is defined by: $v_a = x / \Delta t_a$ (4), where $\Delta t_a = t_{a2} - t_{a1}$, the difference of radiocarbon ages found in two observation wells (1 and 2) beeing on the same flow line at a distance **x**.

There are three great problems that the radiocarbon method is facing:

1. the difficulties in determining the initial concentration (c_o) of tracer at the entrance to the system;
2. the isotopic exchange reactions during the underground mouvement of water;
3. the retardation resulting from matrix diffusion.

All the three above mentioned causes lead to overestimations of the ages ($t_a > t_w$) and implicitely to underevaluation of the velocities ($v_a < v$).

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Stimulated by the necessity of using valid data in the mathematical modelling, the problem made the object of recent, deeper preocupations, as Ph. D. papers (MALOSZEWSKI, 1994) or even at the level of IAEA advisors (ZUBER, 1994). The existing data were reassessed and systematized and certain attempts were made to quantify the errors introduced by the method. At the present knowledge stage, it is known that:

The correction of c_0 is made by various methods: empirical, chemical, isotopic or mixted ones (FONTES and GARNIER, 1979), largely used now even by specialized geochemical programmes. Almost all radioisotopic ages existing today in the literature have been corrected only for c_0.

The diminishing of the effects caused by isotopic exchange reactions can be achieved by applying a retardation factor, including the instantaneous exchange reactions (R_{ap}) as well as the kinetic ones (R_{ak}): $R_a = R_{ap} + R_{ak}$ (5). As it is difficult to determine for each case, it can be admitted that $R_a \cong 20$.

A number of recent studies have shown that stagnant water in the micropores of the matrix material of fissured rocks is an important hold-up reservoir for solutes transported by mobile water in fissures and fractures. The delay of the solute movement is caused by diffusion exchange between the fissures and matrix. This delay may be deduced from: $R_p = (n_p + n_f) / n_f$ (6), where n_p is the matrix porosity and n_f - fissure porosity. Although tritium and the stable isotopes of oxygen and hydrogen are considered as ideal tracers for the groundwater, the retardation phenomenon caused by the diffusion through the matrix affects them as well.

The estimation of the total retardation factor **R**, including R_p as well R_a, can be done by relation: $R = (n_f + R_a * n_p) / n_f$ (7).

As a theoretical concept, $R = t_a / t_w$, which means that the retardation factor is the value with which the radioisotopic age must be corrected in order to obtain the actual age of the water. For a rock with moderate porosity ($n_p = 0.05$ and $n_f = 0.01$), $R = 100$, fact which means that the radioisotopic age is two magnitude orders higher than the real age of the water.

III. Stage of the knowledge on South Dobrogea.

The following refer only to the Mesozoic ($K+J_3$) aquifer, named still *Lower aquifer*.

Geological background. This aquifer is mainly related to the Jurassic limestone and dolomitic deposits, sometimes tectonized and karstified; in most parts of the region it represents a unitary complex, except for the area of Tuzla horst where this one lacks and the waters "migrate" in Cenomanian deposits and in the northern part where the Jurassic and the Barremian aquifers are separated by Neocomian (marls and clays) deposits. The thickness of the whole complex gradually decreases from the SW to the E and NE, from above 1,000 m to 400 m.

Hydrogeological / isotopic knowledge. There are three reference moments in this process; they will be referred to according to the year their results were published: 1975, 1987, 1994.

Moment 1975 (TENU et al., 1975): for the first time in Romania, ^3H, D, ^{18}O, ^{13}C and ^{14}C were determined simultaneously for few wells in this area. These data, their areal distributions and comparison with the surface-water isotopic contents, have shown the first elements of a conceptual model (the recharge area on the south-western side of the region, the flow direction WSW - ENE and velocities of about 3.0 to 7.0 m/year).

Moment 1987 (TENU et al., 1987): is a result of 3-year research contract sponsored by IAEA. This study deals mainly with isotopic research but is subtantiated by interpretations of structural geology and hydrogeology. The first regional piezometric map (levels before 1975) was carried out. The entire range of analyses mentioned at the previous moment was achieved, but for a larger number of points.

The radiocarbon analyses are from 1982-1983 years, the radiometric ages distribution at this second moment being very similar to those of the 1975 stage: from 1,950 (south-western corner) to 19,100 (Siutghiol Lake zone) and 29,250 (Mangalia) years. A correction of the ^{14}C radiometric ages by means of various methods (Vogel, Pearson and Fontes-Garnier) was performed. All the conclusions reached were synthetized into a conceptual hydrogeological model **(Fig.1)** which complete the first form from 1975.

Moment 1994 (ZAMFIRESCU et al., 1994): refers only to the geological and hydrogeological framework. It brings a better structural image, an attempt to provide each compartment with a set of individualized hydrogeological parameters as well as an up-dated piezometric map.

IV. Discussion and assessment of results.

It must be remainded that radiocarbon can be optimally utilised for age determinations only in steady-state flow systems (MALOSZEWSKI and ZUBER, 1982). In the aquifers were recent exploitations have increased the hydraulic gradients, as it happend during the last years in South Dobrogea especially by putting into function the new catchment of Medgidia, the ages obtained by ^{14}C will most probably be according to the moment before starting the exploitation.

The available radiocarbon results will therefore be discussed in comparison with the before 1975 piezometric image (published in the stage 1987) and implicitely with the conceptual model shown on Fig.1.

A reevaluation of the ages and real flowing velocities of the aquifers was indended by considering all correction method. In this sense, several intervals / reaches of the interest were selected acceptably corresponding to flow lines and having also ^{14}C age determinations at the reach end. The results of the calculation and correction operations are given on **Table I** which is greatly selfexplanatory. The following points must be precised:

- pumping tests made in 1994 by NIMH and Hydrodata - Germany in the area of Medgidia (unpublished results) indicate as maximum transmissivity limit, 100,000 m^2/day; this value seems to be a resonable limit for the entire region in appreciating the hydrogeological parameters;

- the total retardation factor $\mathbf{R} = 101$, was calculated according to equation (7) on the basis of the following partial parameters: $R_a = 20$; $n_p = 0.10$; $n_r = 0.02$. As for the calculation of column 6, $\mathbf{n} = 0.12$.

Because we can not know the "true" real flowing velocities, the discussion and assessment of the obtained values may be done only by comparing the results of the two methods.

① For intervals 2 and 4 located in the central part of the area, on the main groundwater flow direction, there is a remarkable agreement of values; the velocities differ very little even between reaches.

② As for Costinesti - Mangalia reach, we can cosider the results as very good having in view the relativity of the appreciation means for the piezometric head at Costinesti and the avearage hydraulic conductivity under difficult structural conditions.

③ For Independenta - Adamclisi reach, the flow is radioisotopically infirmed. Although hydrodynamically this flowing direction is present also, even more pregnant, in the last years (ZAMFIRESCU et al., 1994) we think the radiocarbon conclusion is true as the hydrodynamic image was obtained in both cases by a forced interpolation of levels.

④ As regarding Baneasa - Alimanu and Pestera - Medgidia intervals, large differences are revealed, up to one magnitude order, between the real velocities calculated by both methods.

On the first reach, special hydraulic conditions are met, fact which could explain the increase of the actual velocities of the water up to the value indicated by radiocarbon, 1,840 m/year. However, this value is aprox. 4 times smaller than the actual velocity calculated by hydraulic method. If we admit $I = 0.6 * 10^{-4}$, the

gradient found in 1994, the value of actual velocity determined by hydraulic method become identical to that isotopically calculated (1,830 m/year and 1,840 m/year, respectivelly). The non-agreement of the values on Table I in this case, probably comes from the unsufficient accuracy of the determination of certain hydrogeological parameters. We appreciate as more trustful the value obtained by radiocarbon.

As concerning Pestera - Medgidia interval, the velocities calculated hydraulically is one magnitude order lower than the one deduced by radiocarbon. Without being able to precise the cause of the non-agreement (probably the level difference of only 0.1 m on a 14 Km length of the reach can cause comments) we appreciate that in this case, on the basis of the comparison with the neighbouring reacahes, the velocity deduced by radiocarbon is more realistic.

V. Conclusions.

1. By the reevaluation of the actual flowing velocities in the Jurassic fissurated-karstified calcareous aquifer in South Dobrogea, by the radiocarbon method, values between 120 and 1,800 m/year were obtained according to the hydrogeological peculiarities of the calculation reach.

2. Although these values are unusually high for a deep regional aquifer, their agreement with the real velocities calculated hydraulically, allow us to believe that they are close to the "true" values.

3. In spite of several restrictions, the radiocarbon dating, as a routine method is very useful and beyond any doubt, for most aquifers including the fissured carbonate ones, if the necessary corrections are done.

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***South Dobrogea*: Comparative table of the actual flow velocities through Lower aquifer, calculated by hydraulic and radiocarbon methods.**

TABLE I.

No.	Interval ❶	Length x (km)	Hydrogeological parameters (hydraulic method) k❷ (m/day)	I*10^{-4}	vD (m/year)	v❸ (m/year)	Hydrogeological parameters (radiocarbon method) Δtar (years)	var❹ (m/year)	Δta (years)	va❺ (m/year)	v❻ (m/year)
1.	Băneasa - Alimanu	20	10,000	2.5	912	7,600	3,800	5.3	1,100	18.2	1,840
2.	Adamclisi - Peştera	19	≅ 2,000	0.9	66	550	6,350	3.0	3,700	5.1	520
3.	Peştera - Medgidia	14	3,000	0.07	8	64	2,550	5.5	2,200	6.4	650
4.	Medgidia - Tortomanu	12	430	6.1	96	800	2,600	4.6	1,500	8.0	810
5.	Independenţa - Adamclisi	19	7	0.9	0.2	2	- 9,700	no	radiocarbon	flow	direction
6.	Costineşti - Mangalia	17	≈ 40	2.6	4	30	2,650	6.4	13,900	♦ 1.2	120

❶ aprox. along the same flow line, according to the hydrogeological map ŢENU et al, 1987.
❷ calculated from the transmissivity values corresponding to the structural compartments (ZAMFIRESCU et al., 1994) and weighted according to their percentual participation in the length of the reach.
❸ v = vD / n, where n = 0.12 (empirical).
❹ var - calculated water velocity according to equation 4 by the difference of radiometric ages, Δtar; rounded values.
❺ va - id., calculated by difference of radioisotopic ages, Δta. Ages corrected for co according to Fontes-Garnier method (♦ corrected by Pearson method).
❻ v - radioisotopic actual flow velocity (corrected for c_e, R_a and R_p ; see the text); rounded values.

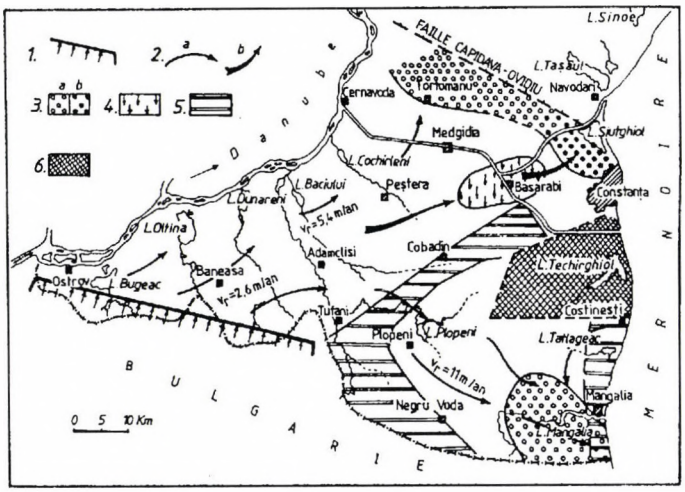

Fig.1 The conceptual flow model of the Lower aquifer from South Dobrogea - Romania (after TENU et al., 1987).

***Key**: 1: the front of the main recharge area; 2a: water flowing direction through the aquifer confirmed by isotopic grounds; 2b: preferrential flowing direction; 3a: natural drainage area of the aquifer; 3b: major drainage area; 4: adventive recharge area; 5: area of low tranmissivities (about 100 m^2/day); 6: the Tuzla - Topraisar horst, an area with lacking (eroded) Jurassic deposits.*

Application of isotopic analyses to study the influence of exploitation of brown coal on the pollution of groundwater

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Keywords: ash-storage, brown coal, groundwaters, ^{18}O, pollution, ^{34}S

Introduction

Ashes coming from power stations are the curse of our times. The ashes contain a lot of harmful ingredients which seep into groundwaters and contaminate them. The ashes contain sulphur compounds coming from combusted coal. Having been oxidated to sulphates, they get into waters. Although sulphates do not belong to the most dangerous compounds, they may be easily monitored. Their presence enables us to observe the infiltration of pollutants into waters. The $\delta^{34}S$ and $\delta^{18}O$ measurements have been used for studying the infiltration of the ash-pollutions into groundwaters in Czech Republic (Smejkal 1979, 1990).

The industrial region of Bełchatów gives a good opportunity for testing stable isotope techniques in tracing of pollution sources. The research was initiated in 1983, only for a narrow practical aspect - a warning against infiltration of the brines from a Permian salt-dome (which cuts brown coal deposit) into outpumped water. The first results were published by Hałas *et al.* (1987).

Study area

Weakly mineralized groundwaters occur down to the depth of 700 m. Their chemical composition is variable. Shallow groundwaters appear at depth of ca. 10 m under the surface in the Quaternary sands and clays. These waters are more variable in their chemistry than deeper waters. Their mineralization varies from 120 mg/l to 3000 mg/l. Deeper waters with mineralization about 300 mg/l are characterized by lesser chemical variability. All of the water horizons have good hydraulic contact. Filtration factors are different, from 2 m/d in the Tertiary rocks to 20 m/d in the Quaternary. Impermeable layers are present too. The drainage system of wells around the Belchatow mine forms a parallel barrier. Some of these wells are 200 m deep or even deeper, up to 400 m. The amount of pumped water exceeds 500 m^3/min. The depression radius is estimated to be 20 km.

The exploitation of the brown coal resources causes major disturbances in the natural environment. Intense dewatering of the exposure area causes extended depression and the disappearance of surface waters. The circulation of groundwaters becomes disturbed. Changes of the waterflow cause further complications. A lot of chemical species may appear in the water. Their concentration may increase. The changes in the groundwater system have been detected by means of 200 piezometres and 2000 wells on the depression area. The reduction of the water table exceeds 10 m. The groundwaters are intensively mixed while pumped up to the depth of 350 m. Deeper groundwaters which lie under this depth are not disturbed, so the admixture of deeper, more mineralized groundwater may be excluded. The side feeding does not

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introduce water of different chemical composition. So, the outpumped water may be utilized to supply tap-water system.

The presence of the salt dome causes another disturbance. The lowering of the water table near the salt dome may cause the infiltration of the brine into the outpumped water. So, careful monitoring of the water is necessary in the wells near this region.

The combustion of coal in the electric power station pollutes environment with gases, dusts and ashes. So far the ashes were washed out from the site of the conflagration and conveyed by water by means of the pipeline system into the sedimentation pools. The ash is stored there while the excess of water seeps down and the pollutant infiltrates into groundwaters. So, the chemical composition of the groundwater and the pumped water is changed and monitoring is necessary. At present, the wet ashes are transported by the conveyor without water and stored in the excavation. This method reduces the penetration of wastes into groundwaters.

Analytical procedures

The water samples were filtered and the sulphate ion was precipitated as $BaSO_4$. For $\delta^{18}O$ analysis the $BaSO_4$ was reduced by the Rafter-Mizutani method (Mizutani 1971) to CO_2. For $\delta^{34}S$ analysis the $BaSO_4$ was decomposed to SO_2, with $NaPO_3$ at 850 °C, by Halas and Wolacewicz (1981) method. The measurements of $\delta^{34}S$ and $\delta^{18}O$ values were obtained with the dual inlet system and triple collector mass spectrometer (Hałas 1979, Durakiewicz and Hałas 1994). Every sample was prepared 2-fold and also measured at least twice in order to obtain better precision of average δ values (presented in tables) than 0.1 ‰ (standard deviation of the average).

Results and discussion

The use $\delta^{34}S$ and $\delta^{18}O$ measurements allows to distinguish between sulphates coming from the dissolved gypsum, those coming from oxidized pyrites and those of antropogenic origin. We have studied $SO_4^{=}$ sampled in the following three areas: (i) the salt dome area, (ii) wells surrounding the ash-pool and (iii) wells near the dry ash storage. The results of measurements are presented in Table I. The samples Nos. 1 - 7 are sulphates from the wells dewatering the salt dome region, Nos. 8 - 16 from piesometers of this area, samples Nos. 17 - 20 represent sulphates from wells surrounding the ash-pool, Nos. 21 - 23 sulphates from wells dewatering the dry storage of ashes in the excavation, Nos. 24 - 28 sulphates from wells dewatering the excavation from the South and the North. The differentiation of the isotopic composition is significant which allows to indentify their origin.

In the salt dome area higher concentration of the sulphates, more than 200 mg/l, may be observed in some of the wells (Nos. 3, 4 and 7 in Table I). These sulphates have $\delta^{34}S$ +10‰ and $\delta^{18}O$ +12‰, typical values for the Permian evaporate. In other wells sulphates have nothing in common with Permian gypsum (samples 1, 2, 5). These sulphates may come from oxidized pyrites or from soil. The sample 6 may be the mixture of sulphates of the evaporitic and the other origin. This well is located between the wells which are presented by samples 5 and 7. The investigation of the isotopic composition of sulphates in these wells is very useful.

Table I. The isotopic composition of sulphates in groundwater from Bełchatów brown coal mine region sampled in November 1994.

Sample No.	Depth (m)	$SO_4^=$ (mg/l)	$\delta^{34}S_{CDT}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)
the salt dome region, wells				
1		42.3	+0.46	-0.35
2		73.6	-0.38	-3.13
3		283.2	+10.71	+12.48
4		214.2	+10.61	+12.08
5		20.1	+0.65	+1.52
6		3.3	+7.48	+8.77
7		199.3	+10.13	+12.01
the salt dome region, piezometers				
8	287	4.3	+35.58	+12.54
9	255	2.5	+27.00	+12.59
10	252	1.1	*not analyzed*	
11	272	91.2	+22.90	+12.52
12	175	3.8	+19.60	+9.85
13	208	1011.4	+11.59	+12.01
14	60	1001.3	+12.87	+12.55
15	141	1471.1	+12.20	+12.57
16	182	9.5	+31.44	+15.08
the ash pool				
17	0	183.4	+1.94	+5.93
18	15	125.0	+3.21	+7.39
19	32	195.8	+1.95	+6.74
20	24	89.3	+3.86	+7.33
the ash storage in excavation				
21		309.6	-0.18	-6.80
22		60.8	-9.03	-5.15
23		161.9	-6.11	-3.47
the wells lying on the edge of the excavation				
24		3.2	+1.92	+5.78
25		9.6	-7.04	-0.45
26		31.3	-0.39	+2.16
27		67.8	+3.04	+6.73
28		15.5	+0.74	+3.42

The piezometers are not good indicators for δ analyses. The values of $\delta^{34}S$ and $\delta^{18}O$ of sulphates Nos. 13, 14 and 15 suggest the evaporitic origin (the $\delta^{34}S$ about +12‰ and $\delta^{18}O$ +12‰), but other results of $\delta^{34}S$ and $\delta^{18}O$ are typical for the reducing process which enriches the sulphates in heavy isotopes. It is hard to say what the primary isotopic composition of these sulphates was like, hence their origin remains unknown. During the reduction the concentration of sulphate decreases and the δ values increase. Such high values $\delta^{34}S$ up to 35‰ and $\delta^{18}O$ up to 15‰ have been

observed together with very low concentration of the sulphate, 9 to 1 mg/l). Probably these groundwaters do not flow fast enough and the stagnancy of the water permits the bacterial reduction of sulphates. Only for the waters in which the concentration of sulphates is high, the values of $\delta^{34}S$ and $\delta^{18}O$ may be unchanged. So, the values of the samples Nos. 13, 14, 15 which present the waters with high concentration of sulphates (more than 1 g/l) are similar to the evaporitic sulphate.

In wells surrounding the ash-pool the concentration of sulphates has increased since the beginning of the storage. The $\delta^{34}S$ +2‰ to +4‰ and $\delta^{18}O$ +6‰ to +8‰ are typical for the antropogenic sulphates and it confirms their origin. The sample No. 17 comes directly from the pool, so it represents the sulphate from ashes. The samples Nos. 18, 19 and 20, which come from the wells surrounding the ash-pool, have a similar isotopic composition.

The sulphates which come from the ash are present in the wells which are situated between the ash-poll and the excavation (samples Nos. 24, 27 and 28). The sample No 25 comes from the well which is situated on the other side of he excavation and has nothing in common with the ash-pool. Indeed, $\delta^{34}S$ and $\delta^{18}O$ are rather typical for oxidized pyrites. Also sulphate No 26 has nothing in common with ash.

In wells near the dry ash storage (Nos. 21 to 23) an increase of sulphate concentration has been noticed, however, the negative values of ^{34}S and ^{18}O exclude the possibility that these sulphates come from the ash. The values are rather typical for the pyrite-oxidized processes. The negative values of ^{18}O suggest that more than 70% of oxygen comes from the water. Such a mechanism is quite probable (Toran 1987, Toran and Harris 1989).

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ISOTOPE GEOCHEMISTRY AND GENESIS OF CARBONACEOUS ROCKS OF UKRAINIAN AND BALTIC SHIELDS

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Keywords : isotope composition, carbon, origin, rare-earth elements, graphite, gneiss, shale, series, facies

Introduction

Carbonic deposits play a significant role in geological sections of Ukrainian and Baltic shields (Golubev et al., 1984; Zahnitko, Lugovaja, 1986). There is a large scientific interest in studing of these deposits as they are important in solving the problem of origin and development of litho- and biosphere. In the last time these deposits attracted the attention caused by discovering the colored, rare and noble metals in them. Besides it is known that the carbonaceous species of these rocks (shungite, graphite) are also valuable useful minerals.

The main scientific and practical problem connected with these rocks is the origin of carbonic species. It is accepted that the most effective approach in this is the isotopic analysis of carbon in thise rocks. It is known that its abiogenic forms are considerably different from biogenic ones by $\delta^{13}C$. Further the isotopic characteristics are also affected by metamorphycal and metasomatical processes.

Results and Discussion

The carbonic deposites of Ukrainian shield are obtained practically on all stratigraphical levels : from early archean to riphean ages. The largest carbon content was obtained in the rocks of early proterozoic age: Buhska, Central-Priazovska and Krivorihska series. Graphitic gneisses containing about 30% of free carbon are obtained, as a rule, in Krivorihska series. They are metamorphised under conditions of granulite and amphybolite facies. In Krivorihska series carbonic deposits are in the form of shales and similitude shungites rocks in which metamorphism is not exceed to epidote-amphibolite facies, more often it is greenschist facies. Isotopic composition of carbon in the samples is summarised in the table 1.

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As it seem, the graphytic gnessis with high grade of metamorphism are characterised by the middle values of $\delta^{13}C$ independently from their age. Generally it is considered as evidence of biogenic origin of carbon.

Carboneous shales of Krivorihska series of Ukrainian shield are characterised with the incresed content of heavy-isotope of carbon, that we consider as evidence of influence of heavy-isotopic metasomatic solutions. It is known that in the section of metasediments of this series these carbonate rocks play the importante role.

The similar affect one can see on the other object of Ukrainian shield also, where carbonate rocks are transformed to diopside-graphites association. The isotopic composition of carbon in this graphite is increased to - 12‰. On contrary, in the case of Kejvska series of Baltic shield, the carbonate rocks are absent, so the transformation of carbon-containing rocks was performed under the influence of light-isotope fluides, that caused the degrease of carbon species in these shales with the isotope carbon-13. It may be also that the some primary degrease of this isotope is caused by the facial peculiarities sediment-formation and some specifity of isotope content early proterozoic biota (Sidorenko, 1991). There are many evidences of such isotope specific deposites of precambrian in the Ukrainian shield.

The rare-earth elements (REE) distribution in carbonaceous rocks are distinguished by their paragenesis. It was revealed that there is some exceeding of light REE relatively to heavy REE with the pronounced Eu-minimum in small-changed clay species of Baltic shield. The distribution of REE is more various without distinct extreme in the samples of graphite gneisses. The variation of REE content (especially light) is increased in the metasomatic-changed rocks. The Sm-minimum sometimes is observed mainly for the rocks where carbon is associated with the amphoteric elements (Mn, Fe et al.)

Conclusion

The performed study permitted us to establish no only the origin of carbon, but the direction of secondery transformations also in the carbonaceous rocks under investigation.

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Table 1

Isotopic composition of carbon in carbonaceous rocks of Ukrainian and Baltic shields

Rock	Stratigraphic position	Contain C,%	$\delta^{13}C_{PDB}$,‰
	Ukrainian shield		
carbonaceous gneiss	Novopavlivsk layer (AR_1)	to 10	-27.2 ÷ -25.3
graphitic gneiss	Buhska series (AR - Pt_1)	to 30	-35.5 ÷ -23.4
graphitic gneiss	Central-Priazovska series (Pt_1)	to 25	- 32.3 ÷ -25.7
carbonaceous shale	Krivorihska series (Pt_1)	to 15	-28.5 ÷ -17.8
	Baltic shield		
carbonaceous shale	Kejvska series (Pt_1)	1 - 3	-42.6 ÷ -25.8

PALAEOWATERS AS ARCHIVES OF FORMER CLIMATIC CONDITIONS

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Keywords: groundwater, noble gases, palaeoclimate, stable isotopes.

Reconstruction of past climates has been attempted from many archives: ice cores and lake sediments, deep sea cores, tree rings, cave deposits etc. In last decades , the studies using groundwater as an archive of palaeoclimate has demonstrated the potential of this approach (Andrews 1992; Rozanski, 1985; Stute et al., 1993). The most informative indicators of climate are stable isotopes of oxygen and hydrogen (18O, D), atmospheric noble gases dissolved in groundwater and conservative ions of meteoric origin. Under favourable conditions, these parameters may be used to reconstruct past temperatures, humidity and atmospheric moisture transport patterns.

Climatic conditions of groundwater recharge may affect its composition in various ways. The oxygen and hydrogen isotope composition of the groundwater is determined by temperature conditions for both, the oceanic evaporation and the subsequent precipitation formation near the site of recharge (Rozanski, 1985).

Most of European aquifers have zones which were recharged under cooler climatic conditions than those at present. This indicates that some of the groundwaters were probably recharged during the interstadial prior to the last glaciation. A strong continental rain-out effect on the isotopic composition is also evident, groundwater becoming isotopically much lighter over continental Europe than over maritime Europe (Andrews, 1993). The isotopic composition of groundwater cannot straightforward determine its recharge temperature because both the recharge under cooler climatic conditions and the continental effect cause a reduction in the heavy stable isotope content. In Europe the slope of the $\delta^{18}O/T_R$ relationship increases from 0.19 (‰/°C) in England to a maximum of 0.43 for the Austrian Molasse and then decreases to 0.26 for the aquifers of the Great Hungarian Plain (Andrews, 1993).

Unusually, low $\delta^{18}O$ values have been found in Estonian groundwaters. Oxygen isotope composition of water in the Cambrian-Vendian aquifer varies between -18.5‰ and -22.7‰ indicating the recharge of glacial water into the aquifer after the last retreat of the Scandinavian Ice Sheet.

Noble gas measurements are needed for an absolute estimate of recharge temperature. The physical principle of the "noble gas thermometer" is the temperature dependence of the solubility of noble gases, especially Ar, Kr and Xe in water (Andrews, 1992). Knowing from laboratory measurements

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the solubility of the individual noble gases as a function of temperature, the observed noble gas concentration in a groundwater sample can be converted into a temperatute at which the water was equilibrated with the atmosphere. In the process of percolating through the unsaturated zone water equilibrates continuously with soil air until it reaches the water table. After entering the saturated zone the water is isolated from the atmosphere. Therefore, noble gas concentrations in groundwater caused by solubility equilibrium reflect the soil temperature at the water table. Variations in the noble gas contents due to seasonal temperature changes are usually smoothed out after a groundwater residence time of some years (Stute, Dean, 1989). As a rough estimate, noble gas concentrations may be assumed to reflect the annual mean soil temperature.

Climate records derived from groundwater have several advantages (Stute et al., 1993). The groundwater system is a low pass filter, i.e. it is not able to record high frequency fluctuations of climate. It also means that the record is not disturbed by short-term events but reflects average climatic conditions on time-scales of the order of several centuries to several thousand years (Stute, Schlosser, 1993). Another advantage of the groundwater archive is that the noble gas thermometer is characterised by a straightforward relationship between temperature and noble gas concentrations and the conversion from concentration to temperature is based on the well-known temperature dependence of the solubility of noble gases in water.

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Garnet Growth in a Limestone - Diabase Sill Contact Zone: a Stable Isotope Perspective.

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Keywords: Contact metamorphism, oxygen isotopes, garnet, marble, diabase, Proterozoic limestones.

Introduction

Small-scale analysis of oxygen isotope zonation in garnets has become a powerful method for interpreting the thermal and chemical evolution of regionally metamorphosed rocks (e.g. Chamberlain and Conrad, 1991). In this study, oxygen isotope zonations of grossular garnet and surrounding marble are examined as potential monitors of thermochemical conditions in a relatively small contact metamorphic zone, that is, a scenario characterized by geologically rapid changes in temperature. Furthermore, the intruded "limestones" are of Proterozoic age and, in parallel to other Proterozoic limestones, have $\delta^{18}O$ values that are much lower than those of younger limestones (e.g.Schidlowski, 1975). Reasons for such low $\delta^{18}O$ values of Proterozoic limestones are debated and interpretations include lower $\delta^{18}O$ values for Proterozoic seawater, post-depositional alteration, or a combination thereof (e.g. Holmden and Muehlenbachs, 1993). Results of the present study, when interpreted together with limestones analyzed distant from intrusives, may help to constraint the extent of alteration experienced by these Proterozoic limestones.

Geologic Setting

The "limestones" investigated are from the Espanola Formation of the Huronian Supergroup, Canada. This Supergroup represents a thick Early Proterozoic sedimentary sequence, whose minimum age is defined by the 2155 Ma Nipissing diabase intrusive. The Supergroup has been of considerable interest to geologists because of its age, its overall low metamorphic grade and exceptional preservation. The Espanola limestone member is, in places, interbedded with siltstones and is interpreted as a shallow marine deposit. "Limestones" consist of recrystallized fine-grained calcite and dolomitic calcite with variable but low contents of organic matter, minor pale-green biotite, quartz and feldspar. In the vicinity of the diabase sill, grossular garnet, vesuvianite and minor diopside occur. These skarn minerals can grow to cm-sized grains along siliceous/argillaceous bands, but their occurrence is confined to impure limestones about 3 to 8m away from the sill contact. Marble in direct contact with the sill consists of almost pure calcite. The siliceous bands consist of very fine-grained quartz, feldspar, and mica in a calcareous matrix.

Analytical Methods

Small chips (1 to 2 mg) of grossular were picked with tweezers from crushed portions of thick sections (about 0.5 to 1mm), inspected for purity, washed in HCl and analyzed by laser fluorination technique (Sharp, 1990). Carbonates were micro-drilled (sample resolution about 100-200 μm) and 0.1 to 0.5 mg of sample was reacted with 100% orthophosphoric acid using an automated "Kiel" device attached to a Finnigan MAT 251 gas source mass spectrometer. For the regional limestone samples, about 5-7 mg of bulk powders were reacted with 100% H_3PO_4 in the conventional way. $\delta^{18}O$ values of grossular and calcite are reported in permil units relative to V-SMOW, while $\delta^{13}C$ values of carbonates are reported relative to PDB.

Results and Discussion

Figure 1a and b demonstrate the typical variability of the $\delta^{18}O$ values of grossular and adjacent calcite on a millimeter scale. Noticeable features include generally constant $\delta^{18}O$

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values in the cores of grossular, but strong depletion of ^{18}O towards grossular-calcite contacts. No gradients in $\delta^{18}O$ are observed when grossular is in contact with the siliceous material ($\delta^{18}O$ about 11‰). Plateau values of different grossular grains range between 8.3 and 9.3‰, irrespective of whether garnet is surrounded by calcite only or is in contact with the siliceous material. Strong depletion in ^{18}O towards the rims suggests retrograde equilibration between garnet and calcite and/or a change in the fluid $\delta^{18}O$ values. $\delta^{18}O$ values of calcite tend to be uniform and average 10.6‰ with $1\sigma=0.32$‰ ($n=22$). In contrast to grossular, no systematic zoning in $^{18}O/^{16}O$ is observed for calcite even though a distinct coarsening of calcite grains can be observed in the grossular-calcite contact zones. These observations suggest that the oxygen isotope compositions of grossular are buffered by those of the volumetrically dominant calcite. Peak temperatures calculated from garnet cores and matrix calcite $\delta^{18}O$ values using the experimental calibration of Rosenbaum and Mattey (1995), which is based on direct grossular-calcite exchange in a dry system, average 800 ± 64°C. Temperatures calculated for grossular-calcite contact pairs average 650 ± 64°C. These temperatures are considered too high for several reasons: i) maximum contact temperatures can be estimated to be 750°C, given regional temperatures before intrusion of 300°C and intrusion temperatures of 1200°C, ii) the presence of vesuvianite (c.f. Labotka et al. 1988), iii) the fine-grained nature of the marbles. Temperatures calculated from a combination of water-based exchange experiments (O'Neil et al., 1969, Lichtenstein and Hoernes, 1992), are much lower, averaging 680 ± 85°C for grossular cores and 510 ± 71°C for rims, and are considered more appropriate.

Figure 2 compares the stable isotope compositions of regional limestones to those of marbles sampled within tens of meters of the diabase sill. It is clear that the two groups have distinct isotopic compositions. Line A-B in Figure 2 further illustrates that simple processes of decarbonation, for any reasonable amounts of decarbonation (the mineralogy suggests that only a few percent of carbonate could have been lost), cannot explain the differences in oxygen nor carbon isotope compositions. Differences between the oxygen isotope compositions of regional limestones and marbles are best explained by processes of fluid-rock interaction with infiltrating fluids derived either from magmatic and/or meteoric sources and/or fluids expelled from the adjacent sedimentary rocks during compaction and metamorphism. Even for fluids of relatively high $\delta^{18}O$ value, that is fluids of magmatic origin or fluids buffered by the rocks in the sedimentary sequence, fluid/rock ratios required to change the $\delta^{18}O$ values by several permil are comparatively small (f/r between 1 and 10) compared to other contact metamorphic aureoles adjacent to acidic plutonic rocks (f/r commonly in excess of 20). Changes in the carbon isotope ratios between regional carbonates and skarn carbonates are more difficult to explain, since it is likely that $X(CO_2)$ values of the fluids have been < 0.1, on the basis of the stability of vesuvianite and grossular within the marbles (Labotka et al., 1988). Low $X(CO_2)$ values would require either very high f/r ratios (> 50) or very low $\delta^{13}C$ values of the fluid (< -7‰). Another factor that may well contribute towards lowering the $\delta^{13}C$ values of the carbonates is enhanced carbon isotope exchange between organic matter and carbonates at elevated temperatures.

Conclusions

1. Grossular-calcite fractionations in a marble-diabase sill contact zone record the thermal evolution of contact metamorphism,
2. Conditions of metamorphism were water-rich and under such conditions, temperatures of metamorphism may be best estimated from grossular-calcite oxygen isotope fractionations made on the basis of mineral-water exchange experiments rather than calibrations based on dry exchange experiments using calcite as the exchange medium.
3. Limestones of the Huronian Supergroup may have experienced significant post-depositional fluid-rock interaction during the intrusion of the Nipissing magmas and their

stable isotope compositions do not represent those of primary Proterozoic marine limestones.

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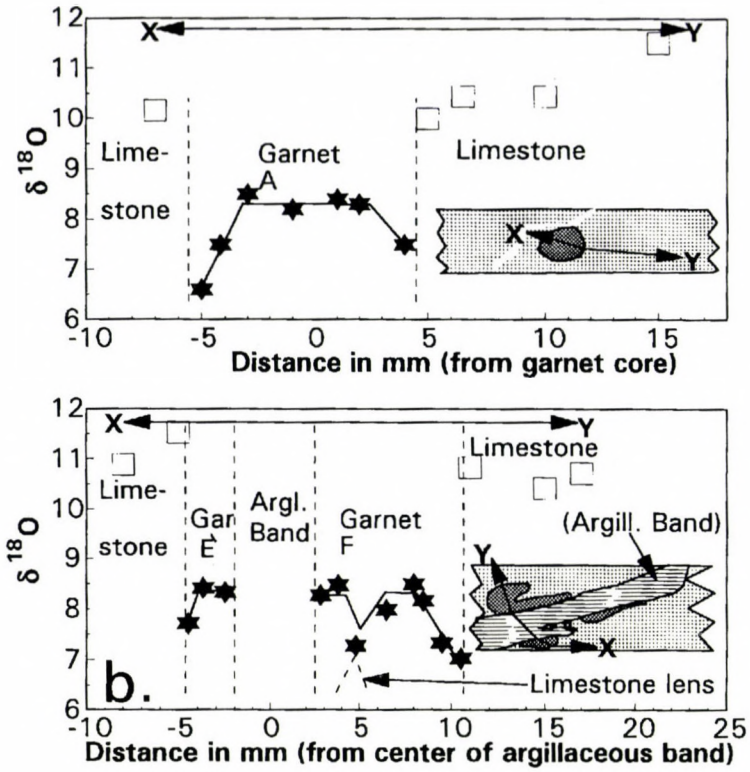
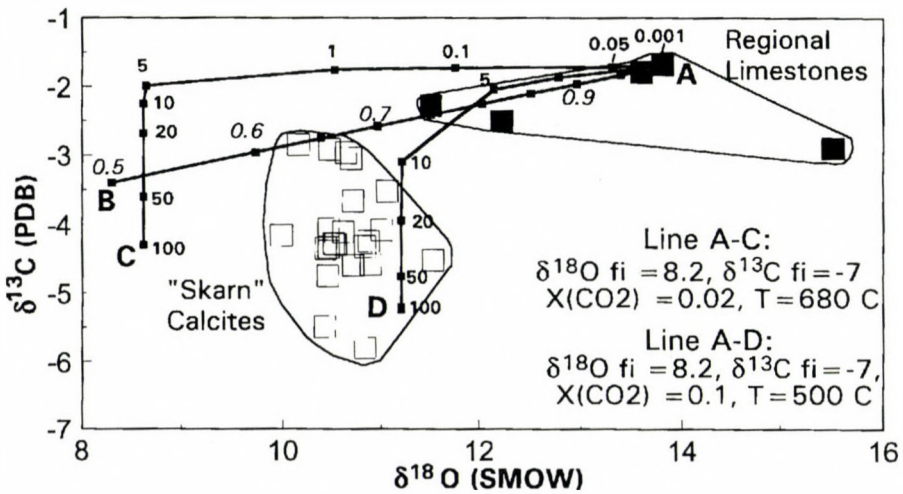
Figure Captions

Figure 1 a, b: Typical oxygen isotope zonation patterns for grossular garnet and calcite on a millimeter scale. Insets illustrate location of sampling traverses (X-Y) on the thick sections used.

Figure 2: $\delta^{18}O$ and $\delta^{13}C$ variation of regional and skarn carbonates of the Huronian Supergroup. Lines A-B, A-C and A-D model changes in the stable isotope composition of carbonates from the Espanola Formation only, through processes of decarbonation (A-B, Rayleigh-type, T=500°C; numbers indicate % of carbonate remaining) and processes of fluid/rock exchange (A-C and A-D; numbers indicate atomic oxygen fluid/rock ratios).


X
Y
Lime-
stone
Garnet
A
Limestone
δ18O
Distance in mm (from garnet core)
Lime-
stone
Gar
E
Argl.
Band
Garnet
F
Limestone
(Argill. Band)
b.
Limestone lens
Distance in mm (from center of argillaceous band)


δ13C (PDB)
δ18O (SMOW)
Regional
Limestones
A
B
C
D
"Skarn"
Calcites
Line A-C:
δ18O fi =8.2, δ13C fi=-7
X(CO2) =0.02, T=680 C
Line A-D:
δ18O fi =8.2, δ13C fi=-7,
X(CO2) =0.1, T=500 C

SULPHUR ISOTOPE RATIOS IN THE LAMINATED TARD CLAY (LOWER OLIGOCENE OF HUNGARY) REFLECT A SALINITY CYCLE.

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key words: sulphate reduction, isotope fractionation, pyrite, diffusion, salinity changes, pore-water

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Bulk of the the sulphur content of marine shales is bound to early diagenetic pyrite produced by bacterial reduction of pore-water sulphate. Bacterial sulphate reduction is accompanied by a substantial sulphur isotopic fractionation. Sulphur isotope ratio in organic rich marine shales often shows variation much stronger than that exhibited by sulphate of contemporaneous sea-water as deduced from isotopic study of marine evaporites. This strong variation reflects changes in conditions of sulphate reduction governing the difference between sulphur isotope ratios of sea-water sulphate and early diagenetic pyrite. Following studies of Berner (1978) and Maynard (1980) extent of fractionation is related to conditions of depositional environment, primarily the rate of sedimentation: the slower is the sedimentation the greater is the difference between sulphur isotopic compositions of pyrite and parent pore-water sulphate. Here stratigraphic variation of the sulphur isotopic composition in the organic rich, pyritic Tard Clay (Lower Oligocene of Hungary) penetrated in the corehole Ad-3 will be reported and its possible cause(s) will be discussed.

The bulk of the sediments studied consist of silts and marls deposited beneath dysoxic-anoxic bottom water as witnessed by their common lamination (Fig. 1). Immature kerogen is of marine origin with some contribution of land plant material (Brukner-Wein et al., 1990). During deposition of the section salinity first continuously decreased below 1.4 % then more saline conditions were progressively restored (Fig. 2).

Total sulphur (S) content was converted to $BaSO_4$ and weighed gravimetrically. The $BaSO_4$ precipitate was used for sulphur isotope analysis following the method of Halas et al. (1982). Results are given in the δ notation relative to the CDT standard. Based on sulphur speciation studies at least

90% of the S is pyrite bound, thus the measured $\delta^{34}S$ values are considered as corresponding to those of pyrite.

$\delta^{34}S$ shows a marked upward increase from -20 to 10 permil in the depth interval between 680 to 645 m then an upward decrease to 0 permil up to 630 m, with an extremely negative (-8 permil) value at 641 m depth (Fig. 2).

In recent marine sediments 30 permil increase in pyrite $\delta^{34}S$ corresponds to an increase in sedimentation rate of at least one magnitude. In view of the relatively constant sedimentological and mineralogical features of the section there are no reason to suppose such rapid changes of rate of sedimentation during its deposition.

An other explanation of the rapid pyrite $\delta^{34}S$ changes would be the evolution of $\delta^{34}S$ of the sea-water sulphate in the relatively closed Tard Sea. Since salinity decrease would led to a slight decrease of sulphate $\delta^{34}S$ rather than to its strong increase, evolution of the sulphur isotopic ratio of the sea-water sulphate accompanying salinity changes would have resulted in a smaller change of pyrite $\delta^{34}S$ than the observed one and in the opposite direction.

Thus it is likely that the pyrite $\delta^{34}S$ changes observed are directly related to evolution of salinity. In absence of bioturbation sulphate supply during early burial was assured through downward diffusion driven by sulphate concentration gradient. In recent brackish water bodies, like Black Sea or Baltic Sea, chloride/sulphate ratio is practically the same as that of the normal sea-water. Thus it is assumed that chloride/sulphate ratio remained constant during deposition of the Tard Clay, in other words sulphate concentration of the Tard Sea experienced changes of the same magnitude as did salinity. In this case it is easy to understand that decrease of salinity then its increase resulted in substantial decrease of diffusive flux of sulphate then its increase during deposition of the Tard Clay. The smaller was the diffusive flux the faster the sulphate supply for a given volume of sediment ceased. In the already closed environment isotopic fractionation due to bacterial sulphate reduction decreased in a kind of batch process resulting in relatively heavy pyrite sulphur isotopic composition. Thus the observed $\delta^{34}S$ pattern is likely related to evolution of diffusive sulphate

supply directly governed by evolution of salinity during deposition of the laminated part of the section.

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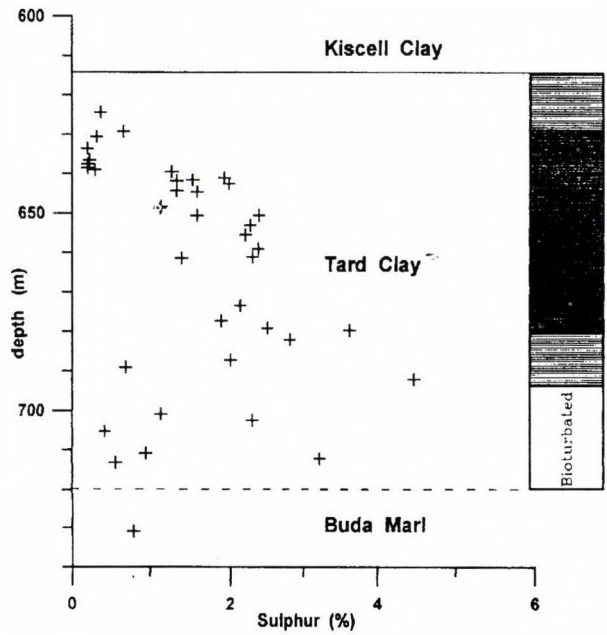

Fig. 1 Plot of sulphur content vs. depth in the Tard Clay section penetrated in the corehole Ad-3 (a part of the data after Brukner-Wein et al., 1990)
In the left-side column more and less dense hatching indicate fine, well developed and partial lamination, respectively.

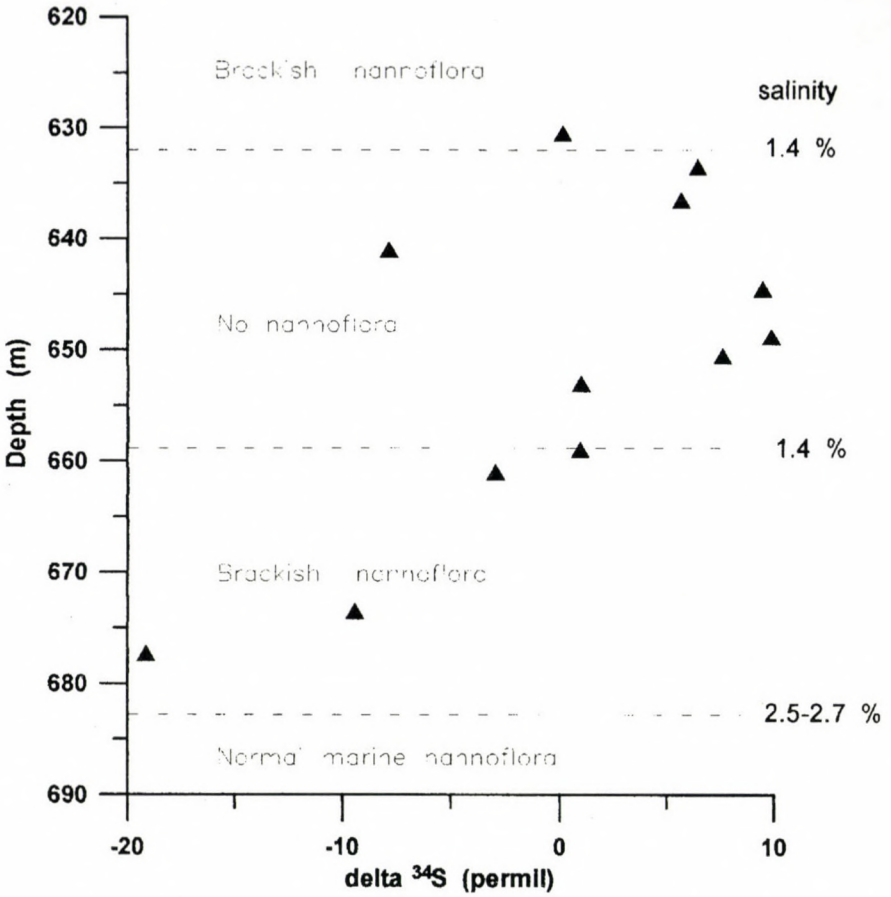

Fig. 2 Plot of sulphur isotope ratio vs. depth in the finely laminated part of theTard Clay section penetrated in the corehole Ad-3 (nannoflora data and salinity estimates after Nagymarosy, 1983)

Radiotracer application for bedload movement study in rivers and nearshore marine zone

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keywords:
isotope hydrology, sediment transport, bedload, radiotracer, tantalum-182, iridium-192

Four version of equipment design and method concept for determination of initial parameters of bedload sediment movement in natural conditions have been presented. Two of them were applied for the measurements at mouth regions of Wisłoka, Dunajec and Raba rivers. The remaining two versions were used in the Baltic marine breaker zone. The bedload tracers used were: Ir-192 in form of sodium free glass grains and Ta-182 in form of wire inserts in the stones from the river bottom. The measured initial parameters of different fractions movement in rivers permitted to choose an optimum theoretical formula on the way of comparison with the transport yield data obtained on the grounds of tracer method proposed by Courtois and Sauzay (Caillot,1983). The measurement carried out in the marine breaker zone allowed to determine the direction , velocity and layer thickness of sediment transport.

Studies of the bedload transport in rivers and nearshore zone of the sea are of great importance for several branches of national economy, especially for river and sea engineering, exploitation of harbours, large artificial water reservoirs and channels.The largest number of existing formula allows to obtain the bedload transport rate on the base of initial parameters of sediment particles movement. The verification of their reliability for natural streams and the choice of the best parameters describe beginning motion.

Radiotracer study in rivers

The classical methods of investigation of the bedload transport rate in natural streams commonly require introduction of traps into flow region. It begins in serious disturbances of the water flow near the bottom layer. Thus the pattern of sediment transport becomes drastically changed. Regarding above it has been decided to adopt radioactive tracer method. Two variants of the measuring method have been developed for investigation of initial phase of bedload transport.

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Variant 1 - "The Rope Bridge" - adequate for investigations on small rivers, fig. 1. It was tested in the Wisłoka river near Mielec (Poland).

Variant 2 - "The Gates" - for big rivers, fig. 2. It was used in the Dunajec river near Tarnów (Poland).

Both variants were successfully adopted in field surveys (Bartnik et al.,1988).
The investigations were carried out on submountain region rivers, in which the bedload sediment consists of wide spectrum of fraction: from fine, sand-like grains through medium gravel up to coarse, stone-like fractions.
In each case, the natural sediment was divided into several fractions characteristic for the bed in the region being investigated. The beginning of the movement of each fraction was observed separately and recorded simultaneously with the hydraulic parameters.
In each of the experiments the tracer used for the fine fractions (d < 10 mm) was Ir-192 in sodium-free glass. For the stones the tracer had a form of tantalum wire (Ta - 182) introduced into genuine stones taken up from the river bottom in the investigated area.
The stones were bored through and tantalum wire inserts put into the holes and fixed with an epoxy resin. The initial activity of a single grain was about 1 MBq .

The counting rate balance of radioactive tracer method has been used to measure the bedload transport in the mountain rivers. The gravely character of bedload implied the study of the representative diameters d_m. The intensity of bedload transport was also calculated by the Mayer-Peter-Muller's formula.

Radiotracer study in the sea

The sea experiments has been conducted in the Coastal Research Station localized on the Polish coast of Baltic Sea. The purpose of this work was to obtain badload transport rate for the different hydro- and meteorology conditions. An inception of sand motion and sediment transport velocity were objective of the experiments too.
The " Spider I" (fig.3) and "Spider II" (fig. 4) - the special constructions were used for determining of initial parameters of motion. The inception of sand movement, current velocity and wave conditions as well as displacement of tracer mass were measured (Owczarczyk et al., 1989). The vertical profiles of radiotracer distribution were determined using core samples. Some results of the experiments will be presented at the conference.

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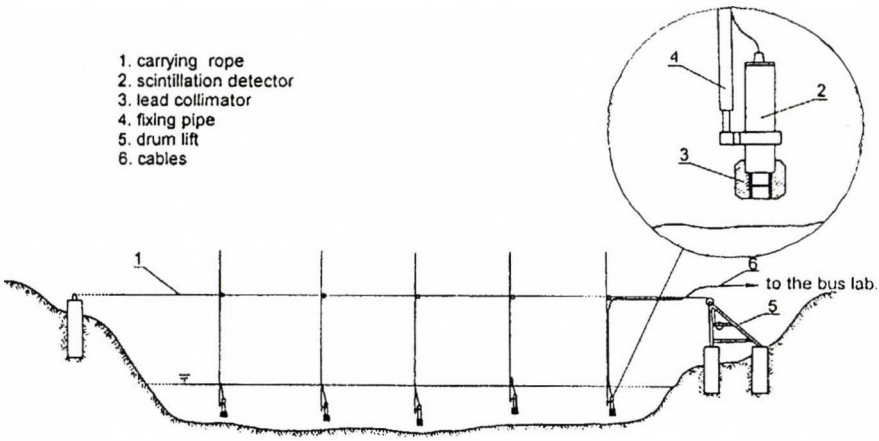

Fig. 1 Measuring arrangement for detection of initial parameters of bedload transport (variant for small rivers).

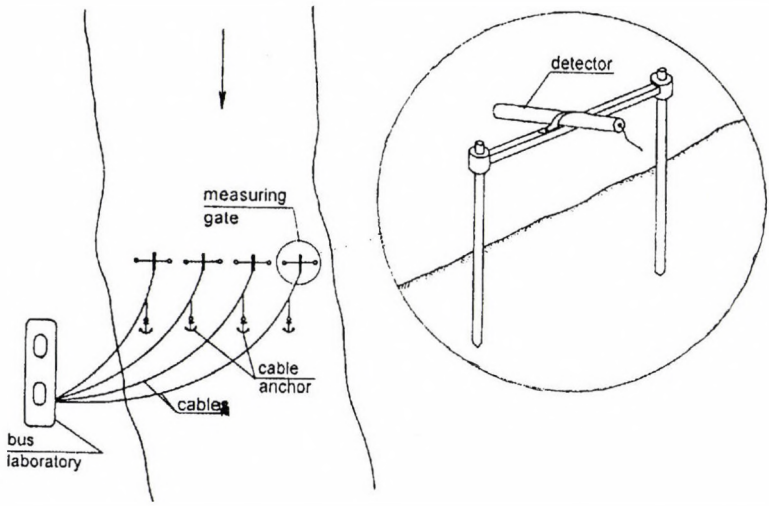

Fig. 2 Measuring arrangement for detection of initial parameters of bedload transport (variant for big rivers).

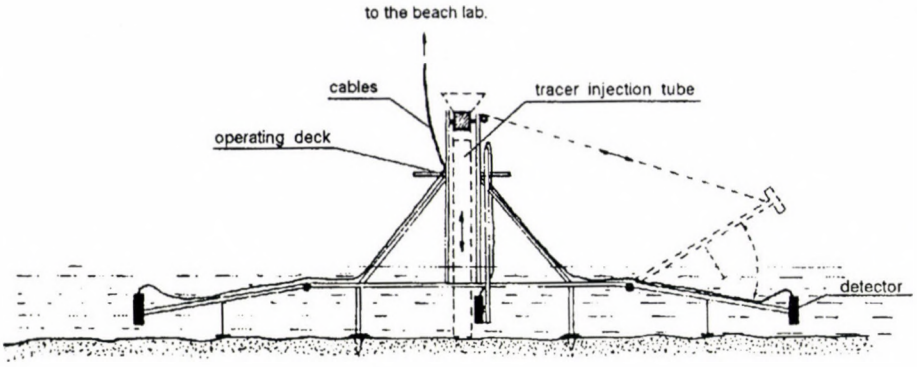

Fig. 3 "Spider I"

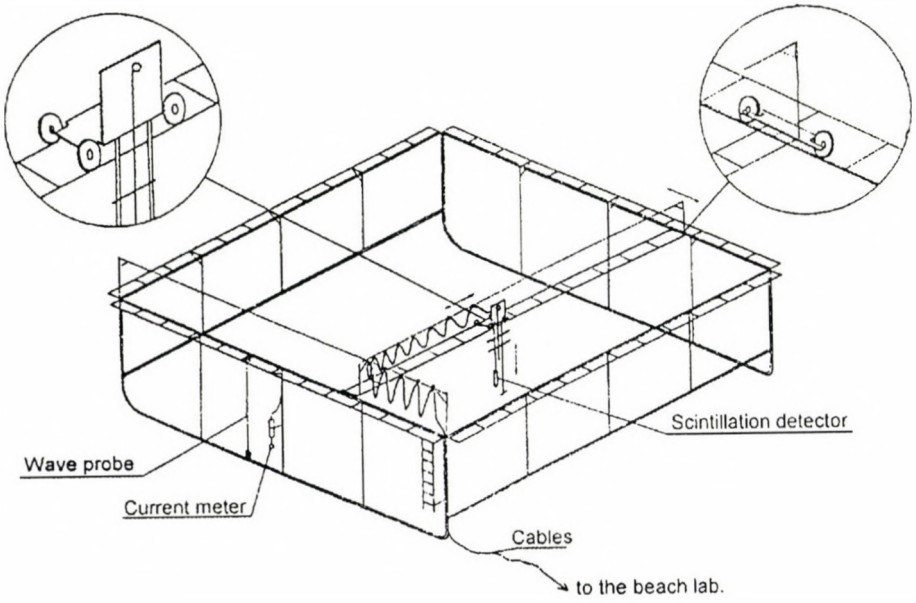

Fig. 4 "Spider II"

Isotopic Geochemistry of Carbonatites and Carbonatitoids of the Ukrainian Shield.

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Key words: carbonatite, stable and radiogenic isotope, Ukrainian Shield.

A presence of a large variety of carbonatic rocks, i.e. sedimentery metamorphic in different drade, metasomatic, hydrotermal-magmatic is a specific feature of the Ukrainian Shield. Isotopic compositions of all these genetic types have usually some specifics but sometimes the ranges of $\delta^{13}C$- and $\delta^{18}O$-values in carbonatic minerals of different groups overlap, each other and genetic identification of the laters becomes rather difficult. It is not therefore always possible to interpret $^{87}Sr/^{86}Sr$-ratios because in Precambrian sedimentary carbonats they are frequently are low and overlap the values of carbonatites. The situation is especially complex in the cases, when carbonatites have been exposed to secondary changes (metamorphic or hydrothermal) or, on the contrary, when the carbonatites them selves interact with metalimestone and mixture of sources of carbonatic substance has place. Such the rock, which are very similar to carbonatites but of obscure genesis are called here carbonatoids. Their isotopic compositions of oxygen and carbon depend on degree and conditions of mixing of deep-seated and of the crust sources.

As an example of carbonatites, which have not been exposed to secondery changes and mixing with sources of crust carbonatic substance, one can consider Chernigovsky carbonatitic complex. In the carbonatites $\delta^{13}C$- and $\delta^{18}O$-values do not as a rule, exceed "Oka-box" limits and $^{87}Sr/^{86}Sr$-ratios are lower than 0.7022. The values of isotopic compositions of oxygen and carbon in carbonats from such the rocks are in range from 8.5 to 18.5% (SMOW) and from -1.3 to -12.5‰, respectively. Ratios of isotops of stroncium do not exceed those of typicall carbonatites.

In every case, especially if data on a distribution of TR

are took in to account, a contribution of the main cources of carbonatic substance to carbonatites can be evaluated. This in carbonatites of Octjabrsky massif an admixture substace of the crust are rather low, and origin of carbonatites is connacted with a repeated intrusion of alkaline magmas and involving of early formed carbonatitic bodies to magmatic activities in crust conditions already.

In Malotersiansky and Proskurovsky alkaline massifs mixing of the deep-seated sources of carbonatitic substance with primary sedimentary one can be observed, therefore their characteristics have the intermediate values too. In primary sedimentary carbonatic rocks, which have been subjected to plastic flows and which have sometimes occurrence a vein form, the primary $\delta^{13}C$- and $\delta^{18}O$- values are seldomly remained, being reduced as a rule to lower ones but randomly run down to values typical of carbonatites.

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Isotopo-Geochemical Feature of Gold-Bearing Deposits of Ukraine.

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Key words: stable isotope, gold bearing ore, genesis, Ukrainian Shield.

Isotopic methods are now inculcated not only to theoretic investigation but also to solving tasks of prospect in concrete regions. For gold-ore deposits are almost always polimetalic ones, there always is a possibility of complex isotopic investigation of them. Intensive application of isotopic methods to ore geochemistry gave apsolutely by new approaches of role and sources of water in hydrothermal ore formations. It is, in particular, shown in the most of publications that there is a vary strong influence of meteoric waters on hydrothermal ore forming systems. Only for two from 40 ore deposits of American continent there is no reason to assume mixing of hydrothermal fluids with meteoric waters. For the others more or less intencive participation of meteoric waters in processes of orogeny has been marked.

The simical conclusions have also been made for some gold ore deposits of Ukraine, for Zakarpatsky ones, in particular. Thus, according to some data, isotopic compositions of hydrogen and oxygen from inclusions of gold-bearing quartz veins show a presence of meteoric water in the inclusions. Our data on isotopic composition of oxygen, carbon and sulphur in ore bodies and country rocks have shown, however, that the water has no relation to ore formation.

Mrtamorphogenic water and CO_2 were here the main ore-forming components have being molilized from country rocks. Meteoric water has realy took a part in mineral forming processes, but at final low temperature stages when is appeared of bearren quartz.

At Muzhievsky ore deposits an isotopic situation is quite different. Here change of isotopic composition of quartz, caused by decrease of $d^{18}O$-values from 11.5 to 5.2‰, along a

development of ore forming process is observed.

Among Precembrian gold ore depocits Klincovsky deposits is studied most completely. Isotopic compositions of oxygen in quartz, carbonates and feldspaths of carbon in carbonates and graphite, K-Ar-age from micas were studied as well as age of zircon. There also are data on isotopic composition of sulfur in sulphides ets.

Isotopic compositions oxygen in quartz and feldspaths were studied along section i.e. from unchanged biotitic gneises, from granite wich intruded ones, from zone of silicification and so on. The distribution of gold along the section is very irregular though some tendencies can be noticed.

If one put the values of $\delta^{18}O_Q$ and $\delta^{18}O_{fh}$ on two exes, he will clearly see two dependences: the first one for unchanged gneises and granitoids and the second one for zone silicification and alteration. Evaluating averaged temperatures it could be found out $620^{+}50^{o}C$ in the former case and lower than $200^{o}C$ in the latter case. It is quite clear that there we are dealing with equilibriums of two temperature conditions, i.e. high temperature one including not only gneises but also granites and some zones, enreached by high temperature quartz, and low temperature conditions where equilibriums have been distroyed because one of the mineral most probably quartz, was a secondary mineral. Exactly in those low temperature associations higher concentrations of Au were detected.

Isotopic composition of carbon in graphite from various accossiations in this series shows that the carbon had been, most of all, of biogenic origin had being, however, strongly treated and, possibly, shifted. Because of that a strong enreachment by heavy isotope ^{18}O have had a place. Isotopic composition of carbon carbonate also indicated an organic primary origin in series of Klincevsky manifestation.

For gold ore deposits of Priazovye there exists some tendency for enreachment by $\delta^{18}O$ samples, where gold quarts ration is higher. A degree of change (opalezation) of quartz might be one of explanations of the tendency. Very high $\delta^{18}O$-values in quarts (up to 18,1‰) are caused by low temperature treatment of quartzite by metamorphogenic water with relatively high content of heavy isotope of oxygen. There also

might be the other explanation that the high $\delta^{18}O$-values to quartz from there quartzite are caused by their primary sedimentary origin. listwenites, beresites and other metasomatites of gold ore deposits of Middle Pridnistrovye were also studied. According to $\delta^{13}C$ and $\delta^{18}O$-values, carbon in carbonates of these metasomatites is, most of all, of deep origin whereas oxygen was of metamorphogenetic origin, indicating, therefore, a mixed character of ore forming fluids.

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DETERMINATION OF THE ANTROPOGENIC INFLUENCES OF CO_2 IN KRAKÓW.

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Key words: carbon dioxide, greenhouse effect, stable isotope composition, antropogenic influences

The contribution of antropogenic emissions of the CO_2 in the greenhouse effect is more complex than was assumed before. The isotopic composition of CO_2 emitted from fossil fuel combustion is not constant and varies with place and time. Determination of this variation has fundamental importance in modelling and well understanding the global carbon cycle and possible climate changes due to antropogenic emission [1,2].

The Kraków town is one of the most polluted regions in Poland. This fact makes possible the measurements of the variability of isotopic composition of CO_2 which is highly influenced by fossil fuel emission [3].

In this paper I present the results of measurement of the atmospheric CO_2 concentration and isotopic composition as well as the method of determination the contribution of CO_2 coming from different sources. The method is based on the analysis of variability in concentration and isotopic composition of carbon and oxygen in the atmospheric CO_2 and assumes fixed values of isotopic composition in biogenic and antropogenic local CO_2. The set of equations describing balace between different CO_2 is resolving for each time step. The effect of calculations is shown on fig. 1. It illustrates the diurnal changes in abundance of CO_2 coming from biosphere, clean areas and fossil fuel combustion. The method is very simple and it can be used in several places to better understand the proceses controling carbon dioxide transport.

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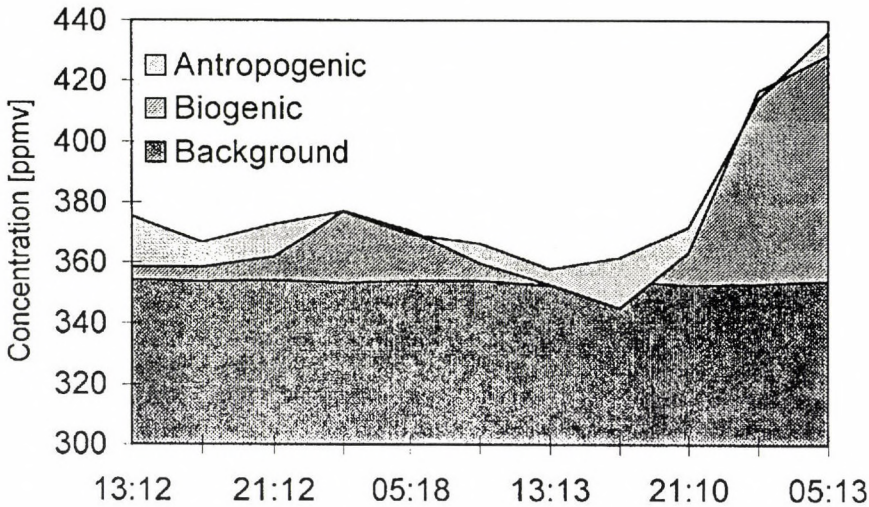

Fig.1. Diurnal variation of the contribution of CO_2 from different sources.

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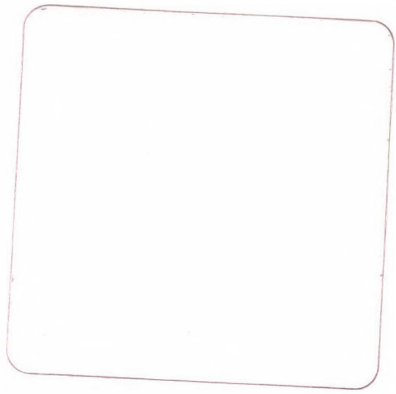

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